ACRP

Web-Only Document 3:

Aircraft Deicing and Airfield Anti-Icing Formulations: Aquatic Toxicity and Biochemical Oxygen Demand

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Prepared in partnership with

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EXECUTIVE SUMMARY

The Airport Cooperative Research Program (ACRP) has sponsored research on environmental characteristics of aircraft and pavement deicers and anti-icers focusing primarily on biochemical oxygen demand (BOD) and aquatic toxicity of formulated products and individual chemical components of formulations. This report presents a background of issues leading to this research, objectives of this document, and a description of the efforts and findings of this research.

Except when the distinction among products is necessary for clarity, "deicer" will refer to aircraft-deicing fluids (ADFs), aircraft anti-icing fluids (AAFs), and pavement-deicing materials (PDMs) generally.

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 provided a base of information to help define the current state of public knowledge regarding deicers.

Federal Aviation Administration and Society of Automotive Engineers Policies Regarding Toxicity and Biochemical Oxygen Demand in Deicers

The Society of Automotive Engineers (SAE) develops and issues the standards for aircraft and pavement deicing materials. The Federal Aviation Administration (FAA) recommends these specifications in Advisory Circulars. SAE provides the only numerical limits related to environmental characteristics, through AMS 1424, which requires Type I fluids to have 50 percent lethal concentrations (LC_{50}s) greater than or equal to 4,000 mg/L for several organisms.[1] 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, six defoamers, nine pH modifiers, five dyes, four oils, and four antioxidants and antimicrobial agents. Not all of these component categories are present in all deicing products; 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. It was therefore concluded that further testing will be needed to define the toxicity of individual candidate deicer components.

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

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 PDM have been improved, four manufacturers have introduced new Type IV formulations in the 2007–2008 winter season, and one manufacturer ha introduced a new Type I formulation for the 2008-2009 winter season with assertions that these 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 studied as extensively. Most research on the fate and transport of deicers has focused on freezing point depressants (FPDs) and, to a lesser extent, on benzotriazole-derived corrosion inhibitors and alkyphenol ethoxylate (APE) surfactants. The components whose environmental characteristics are not well understood include dyes, thickeners, pH modifiers, defoamers, other corrosion inhibitors and surfactants, and even the FPDs used in pavement deicer products.

Degradation rates of FPDs are dependent on environmental factors such as medium, temperature, travel time, and established bacterial communities in soils and receiving waters. Benzotriazoles and APEs have been studied at a small number of airports, but the bulk of research on APEs 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 thei 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 ADF and AAF 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 and glycol surrogates such as chemical oxygen demand (COD) and BOD cannot be used as reliable indicators of additive content in effluents.

Conclusions from current 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 PDM are the FPDs.

Characteristics of Deicers in Wastewater Treatment Systems

The most commonly used FPDs (propylene glycol, ethylene glycol, acetate, and formate) are readily biodegradable under both aerobic and anaerobic methanogenic conditions. Because of the ease by which the 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 be completely biodegraded 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 different treatment strategies have varying effectiveness, 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. Potassium formate– and potassium acetate–based PDMs 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 PDM. It was subsequently found that poorly maintained systems allowed entry of PDMs. Corrective actions and improved products and components have greatly reduced or eliminated the problems.

Reports of pavement deterioration, including degradation and disintegration of asphalt pavements, softening and stripping effects on bitumen and asphalt concrete, and scaling and surface cracking were determined to be a result of alkali-silica reactivity linked to potassium-based pavement deicing and anti-icing formulation (PDF). It was subsequently 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, 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 10 years, 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. has introduced a propylene glycol/glycerol-based Type I ADF that is described as having lower BOD_5 and aquatic toxicity compared to many previous Type I formulations. Battelle has recently released an ADF–AAF and a PDF, both based on glycerol as the primary FPD. Battelle is also working on alternative PDF formulations that are less damaging to aircraft components and less expensive than current PDMs. 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 has developed two versions of Type I fluid using agriculturally based products that were intended to be favorable regarding toxicity and BOD issues. Even though some of these formulations have been certified according to SAE standards, problems involving residue formation, foaming, or unfavorable thickening after application have been encountered during field testing. The prospects for near-term commercial availability of these products are unclear.

Methodological Issues

A number of methodological issues were identified in the literature review.

Biochemical Oxygen Demand Standard 5-day BOD (BOD_5) testing as well as extended length BOD testing pose unique challenges in samples containing deicers. Issues include determining proper dilutions to characterize BOD accurately, properly acclimating microorganisms, and having seeds with insufficient microorganism densities.

Analysis of Additives Standard techniques are not in place for determining deicer additives such as benzotriazoles and APEs. These techniques are currently in flux, necessitating regular review of literature to evaluate the most current methods.

Aquatic Toxicity Acute deicer toxicity test results in low-temperature tests were not dramatically different from those in standard temperatures, with *C. dubia* slightly less sensitive to deicers at lower temperatures and fathead minnows slightly more sensitive to deicers at lower temperatures. One complication when conducting toxicity tests with samples containing deicer is low dissolved oxygen (DO) resulting from high BOD. A successful method for improving DO 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}s averaging about 10,000 mg/L, whereas two products showed LC_{50}s near 30,000 mg/L. Type IV deicer products consistently demonstrated much greater toxicity than the Type I products, with LC_{50}s near 2,500 mg/L and lower. Toxicity results with marine species were similar to those with freshwater test species.

Toxicity in fractionated Type IV and Type I deicer products 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 FPDs.

Four manufacturers introduced new Type IV formulations for the 2007–2008 winter season, one manufacturer introduced a new Type I formulation and one manufacturer introduced a new PDM for the 2008-2009 winter season with claims that these formulations would be more environmentally friendly than past AAF formulations. Research on these formulations is not included in this toxicity analysis.

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 potassium acetate–based liquid PDM, and sodium acetate– and sodium formate–based solid PDMs. Expanded testing was conducted on one formulation of propylene glycol Type I ADF, one propylene glycol Type IV AAF, and one potassium acetate PDF to determine decay rates over a 40-day period at 20°C and 5°C in marine water and freshwater. BOD_5 and COD results are presented in Table ES-1.

TABLE ES-1 Summary of BOD_5 and COD Results for Tested Deicers

		Values as Neat Formulation		Values as Primary Source of Oxygen Demand		
Formulation	**% FPD**	**COD (mg/kg)**	**BOD_5 (mg/kg)**	**Primary Source**	**COD (mg/kg)**	**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.

Biodegradability was examined by comparing BOD and COD results. The degradation percentage was between 40 and 82 percent for six of the formulations. Decay rates in the 40-day test indicate that degradation occurred more rapidly within the first 15 days than during the rest of the test period. At least 78 percent degradation was exerted 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 percent degradation for ethylene glycol products, 61–77 percent degradation for propylene glycol products, and 86–94 percent for acetate-based products. Results of the 5°C marine tests indicated that degradation was significantly less in low temperatures with the propylene glycol ADF and AAF exerting less than 10 percent degradation, and the potassium acetate PDM exerting 69 percent degradation.

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ACRONYMS AND ABBREVIATIONS

µg/L	micrograms per liter
µL	microliter
µM	micromolar
AAF	aircraft anti-icing fluid
ACRP	Airport Cooperative Research Program
AD	Airworthiness Directive
ADF	aircraft-deicing fluid
AMS	Aerospace Material Specification
APE	alkylphenol ethoxylate
APHA	American Public Health Association
ASR	alkali-silica reactivity
ASTM	American Society for Testing and Materials
ATR	attenuated total reflectance
BOD	biochemical oxygen demand
BOD_5	5-day biochemical oxygen demand
BT	benzotriazole
$CaCl_2$	calcium chloride
CAS #	Chemical Abstracts Service registry number
CIC	corrosion-inhibiting compound
COD	chemical oxygen demand
DO	dissolved oxygen
EC_{50}	half maximal effective concentration
EG	ethylene glycol
EO	ethoxymer
EPA	U.S. Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FAA	Federal Aviation Administration
FID	flame ionization detector
FPD	freeze-point depressant
FTIR	Fourier transform infrared
GC/MS	gas chromatography/mass spectrometry
GMIA	General Mitchell International Airport (Milwaukee, WI)
GPC	gel permeation chromatography
HPLC	high-pressure liquid chromatography

IC_{25}	25 percent inhibition concentration
ISO	International Standards Organization
kDa	kilodalton
KgO_2/Kg	kilogram of oxygen per kilogram of product
L	liter
LC_{50}	50 percent lethal concentration
LC/MS/MS	liquid chromatography–tandem mass spectrometry
LRU	line replaceable unit
mg/L	milligrams per liter
mm	millimeter
MS/MS	tandem mass spectrometry
MWCO	molecular weight cut-off
ng/L	nanogram per liter
NMR	nuclear magnetic resonance
NP	nonylphenol
NPE	nonylphenol ethoxylates
OP	octylphenol
OPE	octylphenol ethoxylates
PDF	pavement deicer and anti-icer formulation
PDM	pavement-deicing material
PG	propylene glycol
Q-TOF	quadropole time of flight
SAE	Society of Automotive Engineers
SERDP	Strategic Environmental Research and Development Program
SPE	solid phase extraction
THF	tetrahydrofuran
TIE	toxicity identification and evaluation
TMDL	total maximum daily load
TOC	total organic carbon
TOD	total oxygen demand
TT	tolyltriazole
UV	ultraviolet
UV-VIS	UV-visible spectrophotometry
XC MAS	cross-coiled magnetic angle spinning

SECTION 1

INTRODUCTION

The Airport Cooperative Research Program (ACRP) has sponsored research on environmental characteristics of aircraft and pavement deicers and anti-icers focusing primarily on biochemical oxygen demand (BOD) and aquatic toxicity of formulated products and individual chemical components of formulations. This report presents a background of issues leading to this research, objectives of this document, and a description of the efforts and findings of this research.

Except when the distinction among products is necessary for clarity, “deicer” will refer to aircraft-deicing fluids (ADFs), aircraft anti-icing fluids (AAFs), and pavement-deicing materials (PDMs) generally.

The efforts of this project have included the following:

- A review of regulations and specifications related to the performance and environmental characteristics of deicer formulations
- A review of issues related to the impact that deicers have on aquatic systems and causes of those impacts
- Laboratory testing of current-use deicers to establish benchmark values for aquatic toxicity, BOD, and chemical oxygen demand (COD)
- A review of deicer formulations under development and their relevant performance- and environmental-related characteristics
- A review of operational and infrastructure considerations
- A synopsis of current analytical methods used in environmental characterization of airport deicing runoff
- A toxicity-based investigation of current-use deicers to determine components responsible for toxicity and identify component classes to focus a search for alternative components
- Identification of gaps in knowledge and data pertaining to the above topics

Background

The aviation industry faces a formidable combination of tasks in ensuring the safety of winter flight operations, which includes removing ice and snow from aircraft surfaces, preventing ice and snow from accumulating on aircraft surfaces before takeoff, maintaining ice- and snow-free taxiways and runways, maintaining flight schedules, and minimizing the environmental impact of aircraft and airfield deicer and anti-icer formulations through deicer-runoff management programs. The industry has made steady progress over the past two decades in collecting and containing deicing runoff; however, it is recognized that complete containment of spent deicing and anti-icing fluids is impractical without a significant financial burden. A potentially more practical approach to reducing the environmental impacts of deicers is in reducing BOD and the potential toxic impact of components in the products and, by extension, in discharges to the environment. Deicer manufacturers have made progress to reduce these impacts in formulations within recent years, but BOD and aquatic toxicity in deicing runoff entering receiving waters continues to be a concern.

Freezing -point depressants (FPDs) in ADFs and AAFs are typically propylene glycol (PG), ethylene glycol (EG), or, rarely, diethylene glycol. ADFs and AAFs also contain water and various additives, collectively referred to as the “additive package,” which enhance the fluids’ performance. Classes of chemicals in additive packages include corrosion inhibitors, surfactants, thickeners, dyes, flame retardants, defoamers, and pH buffers.

Although it is recognized that the primary source of BOD in a deicer is the FPD, the source of toxicity is not as clear. Aquatic toxicity in aircraft deicers has been reported to be associated with components of the additive packages (Pillard, 1995), but additive package components are proprietary and considered to be trade secrets. Only two classes of additives that contribute to toxicity have been identified in the literature: Benzotriazoles are corrosion inhibitors that contribute to toxicity in some deicers (Cancilla et al., 1997), and alkylphenol ethoxylates (APEs) are a class of surfactants that contribute to toxicity in some deicers (Corsi et al., 2003). In addition, APEs have the potential to produce degradation products that are considered endocrine disruptors (Servos, 1999). Recent research evaluating component toxicity in ADF and AAF has determined that benzotriazoles and APE are not present in all formulations and account for only a portion of toxicity in deicers where they are present (Corsi et al., 2006a). It appears that the remaining unexplained aquatic toxicity in deicers is due to other proprietary additive components, explaining the need for this project.

The situation with airfield PDMs is similar but not as well defined. The primary FPDs in available PDMs are the glycols, plus urea, and potassium and sodium salts of acetate and formate. All of these chemicals represent significant sources of BOD. The composition of PDM additive packages and their potential contribution to toxicity are poorly understood.

Objectives

The purpose of this document is to present results of an extensive review of information on environmental characteristics, operational and infrastructure issues, and BOD and toxicity testing results. Specific objectives are as follows:

- Define the state of the art with respect to aquatic toxicity and BOD of aircraft and pavement deicers in use at airports in the United States
- Describe issues related to fate and transport of deicers through review of currently available information
- Identify the components of deicers that are responsible for aquatic toxicity and BOD

Report Structure

This report is structured to be generally consistent with the work tasks described in the ACRP 02-01 Amplified Research Plan, dated November 15, 2006:

- Section 2 presents the results of a review of relevant literature and other appropriate data sources.
- Section 3 presents the methods and results used to characterize deicer formulations and components that contribute toxicity and BOD.

SECTION 2

LITERATURE AND DATA REVIEW

The first step in this project was establishing a central repository of references regarding toxicity of ADF components, sources of BOD, environmentally friendly alternatives for ADF components, performance issues, and operational issues. This section summarizes the information in this repository.

FAA and SAE Policies Regarding Toxicity and BOD in Deicers

Requirements, Guidance, and Standards Regarding Toxicity and BOD

Two entities establish requirements, guidance, and standards for aspects of aircraft and pavement deicing, including the products used: the Federal Aviation Administration (FAA) and Society of Automotive Engineers (SAE). FAA has no formal guidance on the BOD content or toxicity of aircraft and airfield pavement deicers. SAE standards for all aspects of aircraft and airfield deicing and anti-icing compounds are described in detail in the Operational Characteristics Testing section (below). The following summarizes how SAE's Aerospace Material Specification (AMS) documents address environmental issues:

AMS 1424 (Type I ADF), AMS 1428 (Types II, III, and IV), AMS 1431, and AMS 1435 provide guidance on environmental testing and reporting of environmental characteristics (summarized in Table 2-1); the same documents provide the following general guidance on levels of aquatic toxicity of deicers:

> The user shall ensure that the fluid meets all local, state, and federal toxicity regulations. The information to satisfy the federal, state and provincial requirements shall be provided by the manufacturer; and for local requirements upon request from the user.

Only AMS 1424 (Type I ADF) cites a specific numerical standard for aquatic toxicity:

> Any Type I deicing fluid shall exhibit Fluid Aquatic Toxicity greater than or equal to 4,000 mg/L. It is the intent of the G-12 Committee to review this standard and revise it upwards to 10,000 mg/L or another appropriate value as data become available that such a value is technically feasible.

TABLE 2-1 Summary of SAE Environmental Testing Standards for Deicers

Environmental Parameter	Aircraft Fluids (AMS 1424 and 1428)	Runway and Taxiway Deicing/Anti-Icing Compounds	
		AMS 1431	AMS 1435
BOD	20°C for 5, 15, and 20 or 25 days	20°C for 5, 15, and 20 days	None
COD or TOD	Results expressed as kg O_2/kg	Results expressed as kg O_2/kg	5-day theoretical TOD expressed as kg O_2/kg
Biodegradability	Results expressed as BOD_x/TOD or COD for all time intervals	Percent biodegradation for 5-, 15-, and 20-day incubation periods. May be approximated by (BOD_x/COD) × 100	Results expressed as percent biodegraded in 5 days at 20°C
Aquatic toxicity	"Formulated fluid shall be tested in accordance with the U.S. Environmental Protection Agency (EPA) (40CFR 797.1300 and 797.1400, revised July 1, 1989) or Organization for Economic Cooperation and Development Guidelines for Testing of Chemicals, Methods 202 and 203 procedures using test species required by regulatory agencies for permitted discharges. Examples include: fathead minnows, daphnia magna, and rainbow trout. The LC_{50} (for fish) or EC_{50} (for invertebrates) concentration (the highest concentration at which 50% of the organisms do not survive the test period) shall be given in milligrams per liter."		

TOD, total oxygen demand; KgO_2/Kg, kilogram of oxygen per kilogram of product; BOD, biochemical oxygen demand; LC_{50}, 50 percent lethal concentration; EC_{50}, half maximal effective concentration.

Characterization of Components in Commercial Deicer Products

Deicing and Anti-icing Products

Deicers are designed to melt ice and snow and wet aircraft surfaces—while being noncorrosive to aircraft and runway materials, being nonflammable, and having low toxicities and low environmental impact. To accomplish these tasks, typical deicers contain FPDs, surfactants, corrosion inhibitors, thickeners, defoamers, pH modifiers, dyes, oils, antioxidants, and antimicrobials.

A literature search was conducted to identify chemicals currently used as components in deicing and anti-icing products. The following sections list chemicals identified through this search.

Freezing-Point Depressants These chemicals significantly lower the freezing point of water, thus melting ice and snow on contact. An FPD typically makes up 40 to 70 percent of the final product as applied, and is typically the main contributor to a product's BOD and a potentially major contributor to toxicity. Table 2-2 lists FPDs that have been reported as being used in deicer formulations.

TABLE 2-2 Freezing Point Depressants

Chemical	CAS #	Reference
1,2-Propylene glycol	57-55-6	Ashwari and Coffey, 1993; Bloom, 1986; Boluk et al., 1999; Hu et al., 1998; König-Lumer et al., 1982; Nieh, 1992
1,3-Butanediol	107-88-0	Lockyerm et al., 1998; Westmark et al., 2001
1,3-Propylene glycol	504-63-2	König-Lumer et al., 1982; Lockyerm et al., 1998
Calcium acetate	62-54-4	Hoenke and Rynbrandt, 1992
Diethylene glycol	111-46-6	Ashwari and Coffey, 1993; Boluk et al., 1999; König-Lumer et al., 1982; Ma and Comeau, 1990; Nieh, 1992
Dipropylene glycol	25265-71-8	Ashwari and Coffey, 1993; Boluk et al., 1999; Nieh, 1992
Dulcitol	608-66-2	Back et al., 1999
Erythritol	149-32-6	Back et al., 1999; Simmons et al., 2007
Ethyl lactate	97-64-3	Sapienza et al., 2003
Ethylene glycol	107-21-1	Ashwari and Coffey, 1993; Bloom, 1986; Boluk et al., 1999; Hu et al., 1998; König-Lumer et al., 1982; Ma and Comeau, 1990
Glycerol	56-81-5	Back et al., 1999; Boluk et al., 1999; Simmons et al., 2007; Westmark et al., 2001
Magnesium acetate	16674-78-5	Hoenke and Rynbrandt, 1992
Mannitol	69-65-8	Back et al., 1999; Sapienza et al., 2003
Pentaerythritol	115-77-5	Back et al., 1999
Polyethylene glycol, mw from 62 to 106	25322-68-3	Boluk et al., 1999
Potassium acetate	127-08-2	Comfort, 2000; Sapienza et al., 2003
Potassium formate	590-29-4	EPA Office of Water, 2000
Proline	147-85-3	Sapienza et al., 2003
Sodium acetate	127-09-3	Comfort, 2000
Sodium formate	141-53-7	Comfort, 2000; Hoenke and Rynbrandt, 1992
Sodium lactate	72-17-3	Sapienza, 2003
Sodium pyrrolidone carboxylate	54571-67-4	Sapienza, 2003
Sorbitol	50-70-4	Back et al., 1999;Sapienza, 2003; Sapienza et al., 2003; Simmons et al., 2007
Triethylene glycol	112-27-6	Boluk et al., 1999; Westmark et al., 2001
Urea	57-13-6	Comfort, 2000
Xylitol	87-99-0	Simmons et al., 2007

Surfactants Surfactants reduce the surface tension of the applied deicer fluids to ensure they completely coat aircraft and runway surfaces. Surfactants may also reduce the adhesion of ice to surfaces making removal easier. Certain surfactants are known to significantly increase a fluid's toxicity. For example, the degradation products of APEs, a class that includes nonylphenol ethoxylates and octaphenol ethoxylates, have been shown to contribute significantly to aquatic toxicity. The concentration of surfactants is typically less than 2 percent by weight. Table 2-3 presents a list of surfactants reported in the literature to be used in deicers.

TABLE 2-3 Surfactants

Chemical	CAS #	Reference
Aliphatic alcohol ethoxylates	—	Ashwari and Coffey, 1993
Brij 35 (polyoxyethylene dodecyl ether)	—	Simmons et al., 2007
Decyl alcohol ethoxylate	—	Corsi et al., 2003
Emerest 2660 (PEG-12 oleate)	—	Westmark et al., 2001
Emsorb 6900 (PEG-20 sorbitan oleate)	—	Westmark et al., 2001
Ethylene oxide / propylene oxide block copolymers	—	Ashwari and Coffey, 1993; Nieh, 1992
Lauryl Alcohol Ethoxylate	—	Corsi et al., 2003
Lauryl alcohol phosphoric acid-ester Ethoxylate	—	Corsi et al., 2003
Nonyl phenol ethoxylate	—	Nieh, 1992
Octyl phenol ethoxylate	—	Nieh, 1992
Oleic acid diamine	—	Bloom, 1986
Oleyl propylene diamine	—	Bloom, 1986
Palmitic acid diamine	—	Bloom, 1986
Siponate A-2466, sodium dodecylbenzene sulfonate	—	Boluk et al., 1999
Siponate DDB-40, sodium dodecylbenzene sulfonate	—	Boluk et al., 1999
Siponate DS, sodium dodecylbenzene sulfonate	—	Boluk et al., 1999
Sodium alkylbenzenesulfonate	—	König-Lumer et al., 1982
Surfonic N-40, 4-mole nonylphenol ethoxyate	—	Ashrawi and Coffey, 1993; Coffey et al., 1995
Surfonic N-60, 6-mole nonylphenol ethoxylate	—	Ashwari and Coffey, 1993; Coffey et al., 1995
Surfonic N-95, 9.5 mole nonylphenol ethoxylate	—	Nieh, 1992
Tergitol TMN-10, branched secondary alcohol ethoxylate	—	Boluk et al., 1999

Corrosion Inhibitors ASM specifications for deicers include standards for effects on materials typically found in aircraft and on runways. These materials include aluminum alloys, high-strength steels, titanium alloys, polycarbonate plastics, copper wiring, carbon-carbon composites, asphalt, and concrete. The choice of FPD often dictates the addition of certain inhibitors (e.g., tolyltriazoles are often added to EG-based fluids to prevent an electrochemical reaction that produces flammable gas). However, because even tap water can contain an amount of dissolved salts sufficient to cause corrosion, inhibitors are likely to be needed in any formulation, regardless of which FPD is chosen.

Often several corrosion inhibitors, each selected for a particular inhibiting purpose, along with chelating agents and solvents, are combined into a single additive package. Some chelating agents include ethylenediaminetetraactetic acid and nitrilotriacetic acid, and some solvents include water, EG, PG, isopropanol, and triethanolamine. The concentration of corrosion inhibitors is typically less than 1 percent by weight. Table 2-4 lists corrosion inhibitors reported in the literature as being used in deicers.

TABLE 2-4 Corrosion Inhibitors

Chemical	CASN	Reference
Benzyltriazole	—	Boluk et al., 1999; Hu et al., 1998; Nieh, 1992
Butyne-1,4-diol	110-65-6	Hu et al., 1998
Cobratec TT-50S, tolyltriazole solution	—	Ashwari and Coffey, 1993
Potassium phosphate	7778-53-2	Moles et al., 2003
Potassium silicate	10006-28-7	Moles et al., 2003
Propargyl alcohol	107-19-7	Hu et al., 1998
Sandocorin 8132, sodium dodecylbenzene sulfonate	—	Boluk et al., 1999
Sodium nitrate	7631-99-4	Hu et al., 1998
Sodium silicate	13870-28-5	Moles et al., 2003
Thiourea	62-56-6	Hu et al., 1998
Tolyltriazole	29385-43-1	Boluk et al., 1999; Hu et al., 1998; Moles et al., 2003; Nieh, 1992

Thickeners Thickeners are used in Type IV aircraft anti-icing fluids, and have been proposed for inclusion in some runway deicing fluids. These chemicals are typically natural or synthetic polymers that increase the viscosity of applied fluids, thus reducing the rates the fluids drain off the applied surface and increase holdover times.

Thickeners are chosen to impart to anti-icing fluids a shear-thinning rheological behavior. While the aircraft is at rest, the fluid’s viscosity is very high. As the aircraft accelerates for takeoff, the shear on the fluid increases, causing a dramatic reduction in viscosity and allowing the fluid to easily shed from aircraft surfaces. The concentration of thickeners is typically less than 2 percent by weight. Table 2-5 presents a list of thickeners reported in the literature to be used in aircraft anti-icing fluids.

TABLE 2-5 Thickening Agents

Chemical	CASN	Reference
Carbopol 1610, polyacrylic acid	—	Ashwari and Coffey, 1993; Nieh, 1992
Carbopol 1621, polyacrylic acid	—	Ashwari and Coffey, 1993; Nieh, 1992
Carbopol 1622, polyacrylic acid	—	Ashwari and Coffey, 1993; Nieh, 1992
Carbopol 672, polyacrylic acid	—	Ashwari and Coffey, 1993; Nieh, 1992
Carbopol 934, polyacrylic acid	—	Ashwari and Coffey, 1993; Nieh, 1992
Carboxymethylcellulose	—	Ma and Comeau, 1990
Cross-linked polyacrylic acid	—	König-Lumer et al., 1982; Nieh, 1992
Hydroxyethylcellulose	9004-62-0	Ma and Comeau, 1990
Iota-carrageenan	9062-07-1	Tye et al., 1987
Kappa-carrageenan	—	Tye et al., 1987
Polyvinylpyrrolidone mw = 10,000–700,000	—	Simmons et al., 2007
Welan gum	—	Westmark et al., 2001
Xanthan gum	—	Lockyerm et al., 1998; Ma and Comeau, 1990; Westmark et al., 2001

Defoamers The surfactants added to ensure adequate surface wetting may also increase the tendency of a fluid to foam. Defoamers decrease the stability of foam, often by increasing foam drainage or decreasing film thickness. The concentration of defoamers is typically less than 1 percent by weight. Table 2-6 presents a list of defoamers reported in the literature as being used in deicers.

TABLE 2-6 Defoamers

Chemical	CASN	Reference
AF-9020, polydimethylsiloxane	—	Hu et al., 1998
DC 1520, silicone antifoam	—	Hu et al., 1998
Foamban	—	Boluk et al., 1999
SAG 1000, silicone antifoam	—	Hu et al., 1998
SAG 7133, silicone antifoam	—	Boluk et al., 1999; Ma and Comeau, 1990
Siltech E-2202, silicone antifoam	—	Hu et al., 1998

pH Modifiers It is typically desirable to have deicers' pH range from 7 to 9. This range can be obtained by using basic chemicals such as sodium hydroxide, potassium hydroxide, or ethanol amines. Buffers may also be used, especially if the FPDs are ionic chemicals. The concentration of pH modifiers is typically less than 1 percent by weight. Table 2-7 lists pH modifiers reported in the literature as being used in deicers.

TABLE 2-7 pH Modifiers

Chemical	CASN	Reference
Diethanolamine	111-42-2	Boluk et al., 1999
Dipotassium phosphate	7758-11-4	Hu et al., 1998
Disodium phosphate	7558-79-4	Nieh, 1992
Monoethanolamine	141-43-5	Boluk et al., 1999
Potassium hydroxide	1310-58-3	Boluk et al., 1999; Hu et al., 1998; König-Lumer et al., 1982
Sodium dihydrogenphosphate	7558-80-7	Simmons et al., 2007
Sodium hydrogenphosphate	7558-79-4	Simmons et al., 2007
Sodium hydroxide	1310-73-2	Ashwari and Coffey, 1993; Boluk et al., 1999; Hu et al., 1998
Triethanolamine	102-71-6	Boluk et al., 1999

Dyes Deicer fluids are color coded for their intended application. For example, Type I fluids are dyed orange, whereas Type IV fluids are dyed green. Numerous dyes are available for use in deicers, including natural and food-grade dyes (Table 2-8). The concentration of dyes is typically less than 0.1 percent by weight.

TABLE 2-8 Dyes

Chemical	CASN	Reference
Eosin orange, tetrabromofluorescein	—	Coffey et al., 1995
FD&C blue #1, alphazurine[a]	—	Chan et al., 1995; Lockyerm et al., 1998
FD&C yellow #5, tartrazine[a]	—	Chan et al., 1995; Lockyerm et al., 1998
Malonyl green, CI acid yellow 24	—	Chan et al., 1995
Shilling green	—	Lockyerm et al., 1998

[a] FD&C Blue #1 and FD&C Yellow #5 can be combined to produce various shades of green.

Oils Several products include small amounts of hydrophobic oils. In theory these oils will migrate to the fluid-air interface and spread out to form a monolayer. Incoming precipitation will then encounter a hydrophobic surface that should help to inhibit dilution of the applied layer of deicer and accumulation of freezing precipitation. If present, the concentration of these hydrophobic oils is typically less than 0.5 percent by weight. Table 2-9 presents a list of oils reported in the literature as being used in deicers.

TABLE 2-9 Oils Used as Hydrophobic Agents

Chemical	CASN	Reference
1-Dodecanol	112-53-8	Lockyerm et al., 1998
Dimethyl polysiloxane (10 to 20 cSt)	—	Ma and Comeau, 1990
Mineral oil (avgC = 15; P = 65%, N = 35%)	—	Hu et al., 1998; König-Lumer et al., 1982
White mineral oil (10 cSt)	—	Ma and Comeau, 1990

Antioxidants and Antimicrobials Some deicers include additives to prevent product degradation through physical, chemical, or biological processes. If present, the concentrations of these chemicals are typically between 0.05 and 0.2 percent by weight. Table 2-10 presents a list of antioxidant and antimicrobial agents reported in the literature as being used in deicers.

TABLE 2-10 Antioxidant and Antimicrobial Agents

Chemical	CASN	Reference
2-Methyl-4,5-trimethylene-4-isothiazoline-3-one	82633-79-2	Simmons et al., 2007
Potassium sorbate	24634-61-5	Simmons et al., 2007
Sodium azide	26628-22-8	Simmons et al., 2007
Sodium sorbate	7757-81-5	Simmons et al., 2007

Toxicity The EPA's ECOTOX database (http://cfpub.epa.gov/ecotox/index.html) was searched for toxicity information for each of the identified commercial components. Table 2-11 shows the values found.

TABLE 2-11 Toxicity Values of Commercial Components as Reported in the ECOTOX Database

Chemical	Function	Species	Toxicity
1,2-Propylene glycol	FPD	Fathead Minnow	LC_{50} 96hr 55,770 mg/L
1,3-Propylene glycol	FPD	Goldfish	LC_{50} 24hr >5,000 mg/L
1-Dodecanol	Hydrophobic agent	Fathead Minnow	LC_{50} 96hr 1.01 mg/L
2-Methyl-4,5-trimethylene-4-isothiazoline-3-one	Antioxidant	Rainbow Trout	LC_{50} 96hr 0.890 mg/L
Butyne-1,4-diol	Corrosion inhibitor	Fathead minnow	LC_{50} 96hr 53.6 mg/L
Carboxymethylcellulose	Thickener	Rainbow trout	LC_{50} 96hr >20,000 mg/L
Diethanolamine	pH Modifier	Fathead Minnow	LC_{50} 96hr 4,710 mg/L
Diethylene glycol	FPD	Fathead minnow	LC_{50} 96hr 75,200 mg/L

TABLE 2-11 Toxicity Values of Commercial Components as Reported in the ECOTOX Database

Chemical	Function	Species	Toxicity
Dipropylene glycol	FPD	Goldfish	LC_{50} 24hr >5,000 mg/L
Disodium phosphate	pH Modifier	Daphnia magna	LC_{50} 48hr 3,580 mg/L
Ethyl lactate	FPD	Zebra danio	LC_{50} 96hr 320 mg/L
Ethylene glycol	FPD	Rainbow trout	LC_{50} 96hr >18,500 mg/L
Glycerol	FPD	Rainbow trout	LC_{50} 96hr 54 mgl/L
Monoethanolamine	pH Modifier	Rainbow Trout	LC_{50} 96hr 150 mg/L
Pentaerythritol	FPD	Daphnia magna	EC_{50} 24hr 38,900 mg/L
Polyacrylic acid	Thickener	Bluegill	LC_{50} 96hr 1,290 mg/L
Polyethylene glycol, mw from 62 to 106	FPD	Rainbow trout	LC_{50} 96hr >20,000 mg/L
Potassium hydroxide	pH Modifier	Guppy	LC_{50} 24hr 165 mg/L
Potassium phosphate	Corrosion inhibitor	Western mosquitofish	LC_{50} 96hr 750 mg/L
Propargyl alcohol	Corrosion inhibitor	Fathead minnow	LC_{50} 96hr 1.53 mg/L
Sodium acetate	FPD	Fathead minnow	LC_{50} 120hr 13,330 mg/L
Sodium azide	Antimicrobial	Rainbow trout	LC_{50} 96hr 2.75 mg/L
Sodium formate	FPD	Bluegill	LC_{50} 24hr 5,000 mg/L
Sodium hydrogenphosphate	pH Modifier	Daphnia magna	LC_{50} 48hr 3,580 mg/L
Sodium hydroxide	pH Modifier	Western mosquitofish	LC_{50} 96hr 125 mg/L
Sodium nitrate	Corrosion inhibitor	Rainbow trout	LC_{50} 96hr 1658 mg/L
Thiourea	Corrosion inhibitor	Daphnia magna	LC_{50} 48hr 9 mg/L
Triethanolamine	pH Modifier	Fathead minnow	LC_{50} 96hr 11,800 mg/L
Triethylene glycol	FPD	Fathead minnow	LC_{50} 96hr 77,400 mg/L
Urea	FPD	Guppy	LC_{50} 96hr 17,500 mg/L
Xanthan gum	Thickener	Rainbow trout	LC_{50} 96hr 420 mg/L

Toxicity data are invariably sparse and inconsistent for these components. However, the available literature values are helpful in identifying components with high and low toxicity values and raise some general questions about how toxicity should be considered when selecting components for new deicers. To evaluate potential environmental impacts, toxicity profiles of components must be compared with the concentrations in deicers and those expected to be found in airport discharges.

As an example of the complexities of interpreting product characteristics, the technical literature for Carbopol polymers (Noveon, 2001), a polyacrylic acid product, states that this toxicity is believed to be caused by "exhaustion"—the polymer thickens the surrounding water to such a degree that swimming becomes difficult or impossible. A similar argument might be made for other polymers, raising the question of how "toxicity" caused by such physical phenomena should be considered. Dilution of these polymers in airport discharge will be such that this type of "toxicity" is not expected to be a factor.

Knowledge and Data Gaps

- Toxicity of additive components used in current deicer formulations
- Toxicity information about other potential components

Characteristics of Deicers in the Environment

The primary environmental (i.e., ecological) concerns associated with aircraft and pavement deicers are those associated with high organic content, which contributes to high BOD, oxygen depletion in receiving waters, odors, and formation of bacterial slimes at stormwater outfalls, as well as aquatic toxicity. Koryak et al. (1998) reported ecological impacts from deicing discharges that included stimulation of dense biological slimes on streambeds, stressing of invertebrate communities in receiving waters, domination by pollution-tolerant *Chironomidae* and *Oligochaeta*, and impairment of resident fish populations. In addition, contamination of groundwater is recognized as a potential issue (Cancilla, 1998; FAA, 1997).

Environmental Information from Manufacturer Literature

Manufacturers of deicers offer information on some environmental characteristics through product literature, such as material safety data sheets and promotional documents. Forty product literature documents from seven deicer manufacturers were compiled, and the environmental characteristics data from these documents are summarized in two tables: Table 2-12, which includes information on aircraft deicing and anti-icing products, and Table 2-13, which includes information on pavement deicing and anti-icing products. Both tables include manufacturer-provided environmental characteristics, such as several different measures of oxygen demand and toxicity. The reported COD, BOD, and toxicity values vary widely among these products. The reader must take care to distinguish between reported results using the formulated product as opposed to reported results of the FPDs without additives. In addition, the reader needs to distinguish between test methods and reporting methods, as they often differ among products.

TABLE 2-12 Summary of Available Information Regarding the Environmental Characteristics of Aircraft Deicing and Anti-icing Fluids

							BOD_5			BOD_{20} (mg/L)		Aquatic Ecotoxicity												
												Acute Toxicity to Fish				Acute Toxicity to Aquatic Inverts			Toxicity to Aquatic Plants					
Brand Name	FPD	Manufacturer/ Distributor	Product No.	Specific Gravity	COD (mg/L)	TOD	Biodegradation or kg O_2 /kg fluid 20°C	kg/L 20°C	2°C	20°C	2°C	Rainbow Trout	Fathead Minnow	Salmon	Freshwater Fish	*Daphnia magna*	*Ceriodaphnia dubia*	Saltwater Mysid	Freshwater Algae	Marine Algae	Toxicity to Microorg.	Chronic Toxicity to Fish	Chronic Toxicity to Aquatic Inverts	Notes
Type I ADF																								
UCAR ADF Concentrate	EG	Dow Chemical Company	—	1.11	1.14 mg/mg	—	69% biooxidation*	0.873	—	96% biooxidation	—	LC_{50}/96 HR 12,400 mg/L	LC_{50}/96 HR 16,300 mg/L	—	—	EC_{50}/48 HR 36,000 mg/L	EC_{50}/48 HR 29,300 mg/L	—	—	—	—	—	—	(a)
UCAR ADF XL 54	EG	Dow Chemical Company	—	—	0.68 mg/mg	—	69% biooxidation	—	—	96% biooxidation	—	LC_{50}/96 HR 12,100 mg/L	LC_{50}/96 HR 27,700 mg/L	—	—	EC_{50}/48 HR 61,200 mg/L	EC_{50}/48 HR 49,800 mg/L	—	—	—	—	—	—	(a)
UCAR ADF "50/50"	EG	Dow Chemical Company	—	—	0.57 mg/mg	—	69% biooxidation	—	—	96% biooxidation	—	LC_{50}/96 HR 23,600 mg/L	LC_{50}/96 HR 30,900 mg/L	—	—	EC_{50}/48 HR 68,400 mg/L	EC_{50}/48 HR 55,700 mg/L	—	—	—	—	—	—	(a)
UCAR PG ADF Concentrate	PG	Dow Chemical Company	—	1.05	1.36 kg O_2/ kg fluid	—	0.731 53% biodegradability	0.742 0.850	—	79% biodegradability	—	LC_{50}/96 HR 20,900 mg/L	LC_{50}/96 HR 6,900 mg/L	—	—	EC_{50}/48 HR 19,200 mg/L	EC_{50}/48 HR 4,280 mg/L	—	—	—	—	—	—	(b)
UCAR PG ADF Dilute "55/45"	PG	Dow Chemical Company	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
KILFROST DF Plus (88)®	PG	Cryotech Deicing Technologies	—	—	0.11 kg O2/kg fluid	—	0.08	—	—	—	—	—	LC_{50}/96 HR (80%) 6,250 mg/L LC_{50}/96 HR (50%) 22,627 mg/L	—	—	LC_{50}/48 HR (80%) 10,000 mg/L	LC_{50}/48 HR 6,700 ppm	—	—	—	—	—	—	(c)
ARCOPlus® Concentrate Type I Aircraft Deicing Fluid	PG	Lyondell Chemical Company	499008	—	—	—	—	—	—	—	—	—	LC_{50}/96 HR 51,400 mg/L	LC_{50}/96 HR 51,600 mg/L	—	EC_{50}/48 HR 43,500 mg/L	—	EC_{50}/48 HR 27,300 mg/L	EC_{50}/72 HR 24,200 mg/L	EC_{50}/72 HR 19,300 mg/L	—	—	—	(d), (e), (f)
ARCTIC Plus® Concentrate Type I Aircraft Deicing Fluid	PG	Lyondell Chemical Company	10961	—	~1,618,000 mg/L	—	—	~0.730	—	—	—	LC_{50}/96 HR 38,000 mg/L	LC_{50}/96 HR 52,000 mg/L	—	—	LC_{50}/48 HR 27,000 mg/L	LC_{50}/48 HR 26,000 mg/L	—	—	—	—	—	—	(e), (f), (g), (h), (i), (j)
OCTAFLO EF	PG	OCTAGON PROCESS, INC.O	—	—	—	—	0.57	—	—	—	—	LC_{50}/96 HR 11,500 mg/L (concentrate); 23,000 mg/L (50:50 dilution)	LC_{50}/48 HR 10,800 mg/L (concentrate); 21,600 mg/L (50:50 dilution)	—	—	LC_{50}/48 HR 14,000 mg/L (concentrate); 28,000 mg/L (50:50 dilution)	LC_{50}/72 HR 13,800 mg/L (concentrate); 27,600 mg/L (50:50 dilution)	—	—		—	—	—	—
OCTAFLO EG	EG	OCTAGON PROCESS, INC.O	—	—	—	1.26 kg O_2/kg of fluid	44% biodegradability	—	—	—	—	—	LC_{50}/96 HR 9,500 mg/L	—	—	LC_{50}/48 HR 2,950 mg/L	—	—	—	—	—	—	—	—

TABLE 2-12 Summary of Available Information Regarding the Environmental Characteristics of Aircraft Deicing and Anti-icing Fluids

							BOD_5			BOD_{20}		Aquatic Ecotoxicity												
												Acute Toxicity to Fish				Acute Toxicity to Aquatic Inverts			Toxicity to Aquatic Plants					
Brand Name	FPD	Manufacturer/ Distributor	Product No.	Specific Gravity	COD (mg/L)	TOD	Biodegradation or kg O_2 /kg Fluid,20°C	kg/L, 20°C	2°C	20°C	2°C	Rainbow Trout	Fathead Minnow	Salmon	Freshwater Fish	*Daphnia magna*	*Ceriodaphnia dubia*	Saltwater Mysid	Freshwater Algae	Marine Algae	Toxicity to Microorg.	Chronic Toxicity to Fish	Chronic Toxicity to Aquatic Inverts	Notes

TABLE 2-12 Summary of Available Information Regarding the Environmental Characteristics of Aircraft Deicing and Anti-icing Fluids

							BOD$_5$			BOD$_{20}$		Aquatic Ecotoxicity												
												Acute Toxicity to Fish				Acute Toxicity to Aquatic Inverts			Toxicity to Aquatic Plants					
Brand Name	FPD	Manufacturer/ Distributor	Product No.	Specific Gravity	COD (mg/L)	TOD	Biodegradation or kg O$_2$ /kg Fluid,20°C	kg/L, 20°C	2°C	20°C	2°C	Rainbow Trout	Fathead Minnow	Salmon	Freshwater Fish	*Daphnia magna*	*Ceriodaphnia dubia*	Saltwater Mysid	Freshwater Algae	Marine Algae	Toxicity to Microorg.	Chronic Toxicity to Fish	Chronic Toxicity to Aquatic Inverts	Notes
Type IV AAF																								
Safewing 2001 Anti-icing Fluid	—	Lyondell Chemical Company	499174	—	—	—	—	—	—	—	—	—	LC$_{50}$/96 HR 51,400 mg/L	LC$_{50}$/96 HR 51,600 mg/L	—	EC$_{50}$/48 HR 43,500 mg/L	—	EC$_{50}$/48 HR 27,300 mg/L	EC$_{50}$/72 HR 24,200 mg/L	EC$_{50}$/72 HR 19,300 mg/L	—	—	IC$_{25}$/ waterflea13, 470 mg/L	(f), (h), (i)
Safewing MP IV 2001 Aircraft Anti-icing Fluid	PG	Lyondell Chemical Company	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(k)
SAFEWING 2012 ANTI-ICING FLUID	PG	Lyondell Chemical Company	8063	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(l), (m)
Safewing MP IV Protect 2012 Aircraft Anti-icing Fluid	PG	Lyondell Chemical Company	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(n)
UCAR ADF/AAF Ultra+	EG	Dow Chemical Company	—	—	0.57 mg/mg	—	49% biooxidation	—	—	99% biooxidation	—	LC$_{50}$/96 HR 380 mg/L	LC$_{50}$/96 HR 370 mg/L	—	—	EC$_{50}$/48 630 mg/L	—	—	—	—	—	—	—	—
UCAR FLIGHTGUARD™ AD-480 PG	PG	Dow Chemical Company	—	—	—	—	—	—	—	—	—	LC$_{50}$/96 200 mg/L	LC$_{50}$/96 HR 375 mg/L	—	—	LC$_{50}$/48 HR 250 mg/L LC$_{50}$/48 HR 225 mg/L	—	—	—	—	—	—	—	(o)
KILFROST ABC-S®	PG	Cryotech Deicing Technologies	—	—	835 mg O$_2$/g	—	—	—	—	—	—	—	—	—	LC$_{50}$/96 HR >1,414 mg/L	LC$_{50}$/48 HR >1,131 mg/L	—	—	—	—	—	—	—	(k), (p)
MAX FLIGHT 04	PG	OCTAGON PROCESS, INC.	—	—	—	0.78 kg O$_2$/kg of fluid		0.520	—	0.785 kg /L	—	—	LC$_{50}$/48 HR 1,975 mg/L	—	—	LC$_{50}$/48 HR 975 mg/L	—	—	—		—	—	—	—

*(BOD/Thod) × 100 = percent biooxidation.
(a) Readily biodegradable and relatively harmless to aquatic life.
(b) Concentrate and aqueous dilutions are readily biodegradable and relatively harmless to aquatic life. Collection and treatment, including glycol reclamation, of spent aircraft deicing and anti-icing fluids are recommended.
(c) Does not contain nonyl phenol ethoxalate surfactants.
(d) No toxicological information was available for this product so PG is used as the surrogate to come up with toxicity values.
(e) Under anticipated conditions of normal use, application of this material as a deicing fluid results in its release to the environment.
(f) No adverse environmental effects accompany this release based on quantity of release and prevailing conditions.
(g) Meets SAE AMS 1424.
(h) Readily biodegradable in aerobic conditions.
(i) There is evidence that it is degraded under anaerobic conditions.
(j) This material is not expected to bioaccumulate (BCF < 1.5).
(k) Meets SAE AMS 1428.
(l) Normal deicing operations involve routine environmental releases with no expected harm to the environment.
(m) PG is expected to degrade rapidly in the vapor phase by reaction with photochemically produced hydroxyl radicals. It has an estimated half-life of 32 hours in an average ambient atmosphere. PG is expected to degrade relatively rapidly via biodegradation in water. It is not expected to be susceptible to hydrolysis, oxidation, volatilization, bioconcentration, and adsorption to sediments.
(n) Meets SAE AMS 1428C.
(o) Readily biodegraded in both surface water and conventional wastewater treatment plants. However, large discharges of these or any other readily biodegradable substance could result in a temporary reduction or depletion of dissolved oxygen levels in the receiving waterways with potential adverse effects on aquatic life. Low winter temperatures and increased dilution from stormwater flow during periods of use generally tend to minimize any adverse effects on dissolved oxygen levels and aquatic levels.
(p) BOD 7 418 mg O$_2$/g.

TABLE 2-13 Summary of Available Information Regarding the Environmental Characteristics of Pavement Deicing and Anti-icing Fluids

							BOD$_5$			BOD$_{20}$		Aquatic Ecotoxicity												
												Acute Toxicity to Fish				Acute Toxicity to Aquatic Inverts			Toxicity to Aquatic Plants					
Brand Name	FPD	Manufacturer/ Distributor	Product No.	Specific Gravity	COD (mg/L)	TOD	kg O_2 /kg fluid, 20°C	kg/L, 20°C	2°C	kg O_2 /kg Fluid 20°C	kg O_2 /kg Fluid 2°C	Rainbow Trout	Fathead Minnow	Salmon	Freshwater Fish	*Daphnia magna*	*Ceriodaphnia dubia*	Saltwater Mysid	Freshwater Algae	Marine Algae	Toxicity to Microorg.	Chronic Toxicity to Fish	Chronic Toxicity to Aquatic Inverts	Notes
CRYOTECH E36® LIQUID RUNWAY DEICER	PA	Cryotech Deicing Technologies	E36 LRD	—	COD (TOD): 0.3 g O_2/g	—	0.14	—	—	0.3	0.3	—	—	—	—	—	—	—	—	—	—	—	—	—
Cryotech NAAC® Deicer	SA	Cryotech Deicing Technologies	—	—	COD (TOD): 0.78 g O_2/g	—	0.58	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Octagon Octamelt PG/KA	PG/PA	OCTAGON PROCESS, INC.	—	—	COD (TOD): 0.73 g O_2/g	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(a)
Octagon RD-1426	PG/ urea	OCTAGON PROCESS, INC.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(b)
Octagon RD-1435	PA	OCTAGON PROCESS, INC.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(a), (c), (d)
PEAK® PA Runway Deicing Fluid	PA	PEAK®	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(e)
PEAK® SF Runway Deicer	SF	PEAK®	—	—	COD (TOD): 0.21 g O_2/g	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(d), (f)
ORD 2000 PG/ Urea	PG/ urea	Old World Industries, Inc.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(g)
Urea	Urea	—	—	—	1.87 g O_2/g	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	(g)

PA, potassium acetate; SA, sodium acetate; PG, propylene glycol; SF, sodium formate.
(a) Does not contain urea or potassium formate.
(b) Contains PG and urea. Conforms to FAA approved specification SAE/AMS 1435.
(c) Contains PA.
(d) More than 90% biodegradable.
(e) Contains a triozole-free corrosion inhibitor, so that it is 100% non-toxic. PEAK® PA meets the requirements of AMS 1435A. Readily biodegradable with low COD/BOD and aquatic toxicity.
(f) Meets the performance and ecological requirements of SAE AMS 1431B. Nitrogen and phosphate-free. Low BOD.
(g) Meets the requirements of SAE AMS 1435. Biodegradable in both surface waters and wastewater treatment plants.

Fate and Transport of Deicers

An understanding of the mechanisms by which deicing products travel across the airport landscape and through the environment is necessary to fully understand their environmental implications. Deicers may follow several different fate and transport pathways after being applied. At many airports, a portion is collected and treated or recycled while another portion is discharged to surface waters via stormwater. The remaining fraction is lost to various processes and mechanisms (Mericas, 2005; Skjefstad, 2005; EPA Office of Water, 2000). Mechanisms that contribute to these losses include plowing to snow banks, evaporation, wind drift, jet blast, absorption into pavement surfaces, seepage into the soil and groundwater through pavement joints and unpaved areas, and tracking by aircraft and ground support vehicles. As a consequence of these transport and loss mechanisms, a significant fraction of the applied deicers is uncollectible through deicer management practices.

The fate of uncollected deicer varies depending on the transport pathways and environmental conditions specific to each airfield setting. Deicer components, especially the FPDs, are generally soluble in water and move freely through the hydrologic system in surface and groundwater. In addition, most deicer components are readily degradable. Most uncollected deicers will therefore be diluted and eventually degraded. The rate at which this happens is highly dependent on environmental conditions. Fate of the additive components is more uncertain because some are unknown, and for those that have been identified, limited environmental information is available.

Transport Canada sponsored a series of research investigations to support development of a model that tracks the dispersal of aircraft ground deicing and anti-icing products for any given airport from the time the products are applied to beyond the departure of the aircraft. Reports with data and quantified characterizations have been published on tracking (Dawson, 2005a), jet blast (Dawson, 2005b), and dripping (Ruggi and Moc, 2005). Tables of fluid displacement distances for different aircraft and engine configurations indicate that jet blast moves spent deicing fluid distances of up to 300 feet (91 m), with under-wing-mounted engines resulting in the greatest displacement. Guidelines are provided to calculate the amount of glycol dripped from start of taxiing through entry of the departure runway for takeoff on the basis of the type of fluid sprayed, the area sprayed, and the ambient weather conditions. Estimation of the amount of glycol tracked away by aircraft and ground support vehicles is described as a function of the type of fluid, surface area, condition (i.e., wet or dry) of the tires, runoff collection operations, and distance traveled. Upwards of 3 L of Type I and 8 L of Type IV fluids can be tracked out of the immediate deicing area by the largest ground support vehicles under optimum conditions. Similarly, as much as 11 L of Type I and 22 L of Type IV fluids can be tracked away by a 747-400 aircraft. Obviously, distance traveled and destination affect the fate of this material. Considerably less fluid was observed to be tracked by smaller vehicles and aircraft.

An earlier Transport Canada report describes the distribution of AAF on and adjacent to runways at takeoff (Merkl, 1995). The key observations included significantly further drift of Type I than of Type II droplets, variable influence of cross winds on Type II deposition on runways, and decreased deposition of Type II fluids on runways with larger aircraft.

Mass balance data in the literature included aircraft deicers but not pavement deicers. Available mass balance–monitoring results suggest that onsite losses may account for between 20 and 75 percent of applied aircraft deicers, depending on the site-specific environmental conditions and infrastructure configuration.

At Baltimore-Washington International Thurgood Marshall Airport, or BWI, daily monitoring data collected between 1998 and 2006 indicate that glycol discharged to surface waters ranged from 4 to 24 percent of total volume applied and averaged 10 percent (Williams, 2006). The fraction of glycol that was neither collected nor discharged in stormwater averaged 19 percent over this period, and ranged from 2 to 36 percent.

Comprehensive mass balance monitoring at Detroit Metropolitan Wayne County Airport indicates that 37 to 48 percent of the BOD in applied aircraft and pavement deicers goes unaccounted for (Wagoner, 2006).

A 4-year study of airport snow banks and snowmelt was conducted from 2000 to 2003 at General Mitchell International Airport (GMIA) in Milwaukee, Wis. (Corsi et al., 2006b). A mass balance analysis indicated that approximately 10 percent of applied ADF and AAF remained in the snow bank directly after the application event, between 25 and 28 percent was recovered by the containment system, between 2 and 24 percent was discharged to a receiving stream, and between 47 and 62 percent of applied fluids was unaccounted for.

A 2-year study of annual surface water loadings for Dallas–Fort Worth International Airport indicated that between 10 and 35 percent of applied aircraft deicers was discharged to receiving water, with an annual average of 15 percent (Corsi et al., 2006c).

Each of the airports in these mass balance estimates included some degree of deicer runoff management in operation during the study, and as a result, the data do not reflect airports without deicer runoff collection systems in place.

Examination of degradation rates of aircraft and pavement deicers on pavement surfaces at cold temperatures suggests that between 13 and 33 percent of a typical combination of deicers may be lost in runoff over a 5-day period, depending on temperatures and rate of applications (Revitt, 2003). Zanoni (1967) describes a modified form of the classic Arrhenius equation temperature adjustment for decay rates that has applicability to modeling BOD decay at low temperatures. This study was conducted on conventional wastewater treatment plant effluent.

Descriptions of the degradation of aircraft deicers and additives in soils and groundwater were found in several articles. There is good evidence that natural attenuation of glycols occurs in groundwater, although there is also some indication that bioclogging and reduction in hydraulic conductivity may occur (Bielefeldt et al., 2004; Klecka et al., 1993). Johnson (1997) reported that biodegradation occurs faster in high clay soils than in sandy soils, and PG may degrade faster in the presence of tolyltriazoles. Gooden (1997) noted that glycol degradation rates may be inhibited by limitations in nutrient (i.e., nitrogen and phosphorus) availability.

Degradation of glycol in receiving streams has been documented as well. Monitoring at outfalls from Dallas–Fort Worth International Airport and in the receiving stream indicated that in-stream degradation ranged from no measurable difference in glycol loadings between the sites to 37 percent reduction in glycol in the 4-km stream reach between the airport outfall and the monitoring site (Corsi et al., 2006c). Differences in degradation were a result of water temperature variations among monitoring events and variability of travel time between sites due to stream flow variations.

In another study, monitoring was conducted at several sites downstream from a controlled release of ADF (Corsi et al., 2001a). Results indicated that in-stream degradation rates were greater than those in laboratory testing (Camp Dresser and McKee Inc., 1997). These differences were likely due to natural in-stream water temperature variations causing different rates of bacterial metabolism, differences between the bacterial populations in the laboratory and field studies, and established populations of filamentous bacteria such as *Sphaerotilus* and *Beggiatoa* that have been observed in abundance on the streambed downstream from the airport but that were absent in laboratory tests.

Fate and transport of identified additives can be substantially different than that of glycol. Certain corrosion inhibitors have high toxicity and slow rates of degradation. Benzotriazole-based corrosion inhibitors have been detected in groundwater (Cancilla, 1998) and in surface water (Cancilla et al., 2003a) that receive airport effluents. Relatively low sorption partition coefficients indicate that benzotriazoles will remain mostly in dissolved phase and will not accumulate in sediments to a large degree (Hart et al., 2004). Riverine studies downstream from municipal sewage treatment plants indicate that some isomers of benzotriazole degrade slowly in the environment whereas others degrade very little and remain in solution (Weiss et al., 2006). Soils on airport grounds in Norway have proven to retain benzotriazoles more than 24 months after deicing had occurred (Breedveld et al., 2003). In addition, uptake of benzotriazoles in fish was confirmed through fish tissue analysis of laboratory exposures and in-stream exposures of fathead minnows (Cancilla et al., 2003b).

Alkylphenol ethoxylate surfactants are of special concern not only because of the toxicity of the parent products but also because of the potential of these compounds to become more toxic through the degradation process. Some of the degradation products—nonylphenol (NP) and octylphenol (OP), for example—are more toxic than their parent compounds (Staples et al., 1998). Some of the degradation products, including NP and OP, are also endocrine disruptors (Staples et al., 2004). Anaerobic degradation is more likely to produce the products with endocrine disruption characteristics. This may have implications for treatment because some wastewater treatment facilities receiving spent deicers use anaerobic digesters.

Results of a snow bank study conducted at GMIA indicated that glycol was selectively removed from the snow banks during melt periods before snow and ice were melted resulting in lower glycol concentrations within the snow after melt periods (Corsi et al., 2006b). Study results also indicated that some of the additives remained in the snow bank after glycol was removed during melt periods. Concentrations of deicer and anti-icer components in airport runoff were similar during periods of snowmelt and during active deicer application periods; however, due to the long duration of snowmelt events, greater masses of glycol were transported to airport outfalls during snowmelt events. Differences in fate and transport of glycol as compared to that of additives shown in this study lead to the conclusion that neither glycol nor COD nor BOD can necessarily be used as a reliable indicator of additive concentrations.

Biochemical Oxygen Demand

Currently available aircraft fluids are based on either PG or EG, and the glycol is the predominant source of BOD. As a result, the BOD contents among aircraft deicing and anti-icing fluids with the same glycol base are similar, with adjustment for glycol concentration (Table 2-12). There is a wider range of FPDs used in commercially available airfield pavement deicers, and the range of BOD is correspondingly varied (Table 2-13). All of these products are biodegradable, and even the lowest BODs found in pavement deicers are substantial. The commonly used products in the United States with the lowest BODs are formulated from potassium acetate and sodium formate. Common environmental concerns resulting from BOD in deicers include low dissolved oxygen (DO) in receiving waters, bacterial growth in receiving waters, and objectionable odors associated with deicer runoff.

Dissolved Oxygen

The magnitude of impact that deicing discharges have on DO depends on the BOD load as well as temperature and physical characteristics of the receiving waters, which determine the capacity to assimilate that load. Unacceptable oxygen depletion may occur where deicing discharges exceed the assimilative capacity of the receiving waters. Generally, colder temperatures result in slower biodegradation and enhanced reaeration, both of which can significantly reduce the impacts of BOD loads. Larger and faster moving receiving waters tend to be able to assimilate larger BOD loads because of the increased availability of oxygen.

Because each setting and situation is unique, site-specific water quality evaluations through DO monitoring and water quality modeling are typically required to quantify how much deicing runoff a receiving stream is capable of safely assimilating without creating a problem with DO. As an example, on the Columbia Slough in Portland, Oregon, investigations into low DO concentrations following winter storms suggested that deicing runoff from the Portland International Airport was contributing significant quantities of BOD to this very sensitive receiving water. Water quality modeling conducted under the Columbia Slough total maximum daily load (TMDL) quantified the relative contribution of all BOD sources in the watershed and led to controls that reduce discharges to the maximum allowable loads. In contrast, at Gerald R. Ford International Airport in Grand Rapids, Michigan, modeling and monitoring efforts proved that regulatory concerns about the impact of deicing discharges on DO in the Thornapple River were unjustified; the river is relatively large, and it was determined to be able to readily assimilate the loads, even without the deicing controls that were subsequently imposed.

Bacterial Growth

Communities of attached bacteria have been observed at or immediately downstream of some airport stormwater outfalls impacted by deicing runoff. The literature often describes these bacteria as “sewer bacteria” or identifies them as *Sphaerotilus natens*, a filamentous bacteria that has been associated with organic-rich wastewater discharges (Quinn and McFarlane, 1988). Often, the attached biomass has an orange color, reflecting iron fixation. These bacterial slimes become a regulatory issue where they are viewed as being “unnatural” biological growth or otherwise an indication of impairment. This type of impairment was the basis for a TMDL for Gunpowder Creek in Kentucky and was the major driver behind stringent controls on deicing discharges from the Cincinnati–Northern Kentucky International Airport.

The occurrence of bacterial growths associated with deicing discharges is not predictable, in large part because the controlling factors are very poorly understood. No research on the specific causes or control of these growths at airport outfalls was found in the literature. An unpublished comparison of water quality characteristics at paired outfalls at the Gerald R. Ford Airport, where 5-day BOD (BOD_5) concentrations are similar but bacterial slimes are seen only at one outfall, led to the conclusion that pH may be a controlling factor (Limno-Tech Inc. and Prein & Newhof, 2006).

The most potentially relevant published research describes the response of *Sphaerotilus sp*. and DO to reductions in BOD loads from dairy and slaughterhouse discharges in New Zealand streams (Quinn and Gilliland, 1988). A particularly significant observation was that different wastes promote bacterial growth at different BOD levels. Bacterial growth was eliminated only when the increase of BOD_5 in the river due to dairy discharges was maintained at 1.8 mg/L or less, whereas higher thresholds were found for primary sewage and slaughterhouse discharges. It was concluded that the very low threshold is the result of low-molecular-weight organics in the dairy discharges. The presence of dissolved and low-molecular-weight BOD constituents was determined to be a better predictor of bacterial growth than total BOD (Quinn and McFarlane, 1988). This observation could partially explain the wide variability in the occurrence of bacterial slimes associated with airport deicing discharges.

Odors

Complaints regarding objectionable odors associated with deicing runoff are common. These odors may emanate from ponds or other open storage facilities, from stormwater inlets, or from outfalls at the airport. Less common are reports of objectionable odors from waters that receive deicing discharges.

Reports of objectionable odors have been linked to propionaldehyde, a degradation product of PG, although hydrogen sulfide and mercaptans created during the biodegradation of deicing chemicals may also contribute to these odors (Gooden, 1997). Empirical evidence suggests that the odors are most commonly associated with aircraft deicing runoff rather than pavement deicers.

The options for mitigating objectionable odors are limited. The available literature does not provide any guidance on critical concentrations of either deicers or their degradation byproducts below which odors will not be generated. A practical mitigation option has been found in using odor-neutralizing compounds dispensed by misters surrounding the source of the odors.

Aquatic Toxicity

Aircraft Deicers and Anti-icers The aquatic toxicity of aircraft deicers and anti-icers has been documented through laboratory studies of the neat fluids (Kent et al., 1999) as well as some of the identified additives (Cancilla et al., 2003b; Cornell et al., 2000; Pillard et al., 2001). Previously observed glycol and COD concentrations indicate that levels associated with aquatic toxicity are periodically present in airport effluents (Corsi et al., 2001b; Novak et al., 2000). In addition, several studies report that bioassay results from samples collected from airport effluents have exhibited significant toxicity at times (Corsi et al., 2001b; Fisher et al., 1995; Hartwell et al., 1995). Toxicity values for currently available deicers from manufacturer literature are reported in Table 2-14. In addition, recent published research provides acute and chronic toxicity test results for five Type I and four Type IV formulations (Corsi et al. 2006a). These results, however, consider the neat fluids before their dilution and introduction into the environment. Fate and transport differences between glycol and additives introduce complications in determining the specific discharge concentrations that have toxicity implications.

Additives, rather than glycol, have been implicated as the primary source of aircraft deicer and anti-icer toxicity (Hartwell et al., 1995; Pillard, 1995). Manufacturers of deicers maintain proprietary additive package formulas and do not reveal the components responsible for toxicity. Researchers have identified two classes of chemical that are of concern with regards to aquatic toxicity in deicers. The first class includes benzotriazole and benzotriazole derivatives (hereafter referred to as triazoles), which are used as corrosion inhibitors in some deicer formulations (Cancilla et al., 1997). The second class of identified additives comprises alkylphenol ethoxylate surfactants, including nonylphenol ethoxylates (NPEs) and octylphenol ethoxylates (OPEs) (Corsi et al., 2003). These deicer components were the subject of recently published research to define the portion of toxicity attributable to publicly identified additives (Corsi, et al. 2006a). In this study, the presence of triazoles was confirmed in five of nine deicer formulations, and the presence of APE was confirmed in five of nine deicer formulations. It was also found that these identified additives account for only a portion of Type I formulation toxicity and for very little of the observed toxicity in Type IV formulations. This observation confirms the existence of other proprietary additives that contribute to aircraft deicer and anti-icer toxicity.

The range of published values for acute toxicity levels of triazoles is between 4.25 mg/L and 118 mg/L (Corsi et al. 2006a; Pillard et al., 2001). A recent assessment of triazoles in the aquatic environment resulted in probable no effect concentrations (PNECs) of 200 μg/L for benzotriazole and 150 μg/L for tolyltriazoles (Wind, 2007). Concentrations in surface water samples associated with deicing discharges have been observed above these levels and have been reported as high as 198 mg/L in groundwater samples (Cancilla, 1998). Overall, few data are currently available for triazoles in airport effluents, and as a result it is difficult to fully assess their potential environmental impact.

The toxicity of APE can be assessed in several different ways. First, the entire APE distribution may be summed to determine total APE concentration and compared against toxic levels. Second, because some individual APE ethoxymers (EOs) are more toxic than others, they must be considered individually. Finally, APE degradation products have toxicity levels different than their parent compounds do, which also requires individual consideration. Toxicity information for the degradation products nonylphenol (NP) and octylphenol (OP) are most readily available in the literature and have been reported to fall in the low milligram-per-liter range, with endocrine disruption also considered to be a factor at these levels (Staples et al., 2004, 1998; Van Miller and Staples, 2005). Toxicity of the parent compounds, alkylphenol ethoxylates, varies according to the EO. Lower level EOs (i.e., those with shorter ethoxy-chain lengths) exhibit toxicity into the low milligram-per-liter range in some cases, whereas higher level ethoxomers exhibit less toxicity (typically greater than 900 μg/L).

Most research regarding the environmental impact of these surfactants has been conducted in the context of treated effluent. In this respect, deicer runoff is unique because it may be released directly to receiving waters without treatment. For this reason, the toxicity of the sum of the entire (undegraded) APE distribution in deicer runoff must be considered. The toxicity of complete distributions of EOs are difficult to assess for specific distributions included in deicer formulations because each formulation uses a different commercial mixture and therefore has a different distribution average "EO number" (i.e., the average length of the ethoxy chain on the base alkylphenol). This ethoxy-chain length distribution is a primary determinate of the formulation's relative toxicity. These APE materials (and indeed all ethoxylated surfactants) are synthesized by base-catalyzed condensation of ethylene-oxide gas on an activated alkylphenol hydrophobe, resulting in polymerization and growth of a polyethoxylate chain. This synthesis typically results in a relatively broad (often Gaussian) distribution of ethoxy-chain lengths present in the resulting product, with the average length approximated by the starting mole ratio of alkylphenol to ethylene oxide. Ethoxyl-chain distributions with greater weight towards lower EO numbers will typically be more toxic than those with higher EO numbers. Few data are available comparing the toxicity of different APE distributions. More work is needed to define this issue, as the limited environmental sample results available for APE in airport effluents indicate that concentrations have periodically approached or exceeded concentrations of concern relative to toxicity (Corsi et al., 2003, 2006b).

Several factors complicate the evaluation of toxicity potential in receiving waters by analyzing glycol or glycol surrogates such as BOD, COD, and total organic carbon (TOC) without directly testing for toxicity:

- Different deicer formulations have different levels of toxicity
- Different ADF and AAF formulations have different concentrations of glycol
- Fate and transport of additives are not necessarily the same as those of glycol

Determining which deicer formulation is present in runoff samples to help evaluate toxicity is complicated. There is currently no reliable method to determine what fraction of deicers present in effluents is due to Type I formulations and what fraction is due to Type IV. Type IV is typically toxic at concentrations at least an order of magnitude less than those of Type I, so the differentiation of formulation types is important. Some deicer forensics analysis has been conducted in studies at Dallas–Fort Worth International Airport and GMIA using a combination of toxicity results, glycol concentrations, and alkylphenol ethoxylate distribution characteristics to indicate deicer type. Through this analysis, it was possible to determine that both Type I and Type IV were present in the effluents studied. It was also possible to determine that Type IV formulations were responsible for toxicity at some times (Corsi et al., 2006c), and that Type I formulations were at least partially responsible at other times. It was not possible to determine the fraction of Type I present as compared to that of Type IV, however. The additives that have been monitored in airport effluents do not provide enough information to distinguish them from all deicer formulations, but they can provide useful insight in some cases. Further identification of unique additives for each formulation would improve this situation and provide a better basis for helping airports identify and quantify contributing sources of deicer loading in discharges. This type of information would be valuable in developing runoff management plans at individual airports.

Airfield Pavement Deicing and Anti-icing Products Deicing and anti-icing products used on airfield pavement have not been studied in as much detail as aircraft deicers with regard to toxicity and level of occurrence in airport effluents. Toxicity data on pavement deicers and anti-icers is generally not provided in manufacturer literature. Ongoing investigations at GMIA are examining the toxicity of selected PDM products compared to concentrations in airport effluent samples (Corsi et al., 2008). Results indicate that FPDs are most likely the primary source of toxicity in acetate- and formate-based pavement deicers, with additives playing a secondary role. Acute toxicity levels for three different test organisms range from 990 to 21,820 mg/L for a potassium acetate product and from 2,870 to 6,370 mg/L for a sodium formate product. Chronic toxicity levels for three test organisms range from 66 to 1,120 mg/L for a potassium acetate product and from 900 to 2,580 mg/L for a sodium formate product. Concentrations of potassium acetate and sodium formate in GMIA effluents are typically less than those of glycols and are widely variable depending on weather conditions. Concentrations of potassium acetate in runoff exceeded the LC_{50} for *P. promelas* (298 mg/L) in 25 percent of samples (n = 60) collected from 2000 to 2007.

Pavement deicing runoff is generally discharged without treatment because of the wide area of application and large volumes of dilute runoff that are involved (EPA Office of Water, 2000). For this reason, pavement deicers and anti-icers will periodically be present in effluents from many airports where airfield deicing is conducted. It is not possible at this time to assess the implications of these discharges on a broader scale with regards to toxicity because of a lack of data availability and the site-specificity of discharge conditions.

Emerging Pollutants

A number of deicer components have not been studied extensively. Consequently, their environmental impact and ultimate fate are poorly understood. Many deicer components, including chemicals discussed above in the Characterization of Components in Commercial Deicer Products section, have yet to be studied in airport runoff. For example, the toxicity profile of alcohol ethoxylate surfactants is similar to that of APE before degradation occurs, but degradation products of alcohol ethoxylates are thought be less harmful than those of APE. The limited data available from environmental studies of alcohol ethoxylates in the aquatic environment has focused on effluent from wastewater treatment, which may not be directly applicable to the context of airport discharge (i.e., degradation and resulting toxicity profiles may differ markedly between these regimes). Similarly, dyes, thickeners, pH modifiers, defoaming agents, corrosion inhibitors, and surfactants—even FPDs used in pavement deicer products—represent classes of chemicals that have not been extensively studied with regard to environmental impact and fate.

Recent Improvements in Environmental Characteristics

Manufacturers constantly consider modifying formulations to improve performance, environmental characteristics, and cost. Several manufacturers have improved the toxicity of Type I formulations in recent years. In 2005, one manufacturer introduced a new Type I formulation that substantially reduced aquatic toxicity from its previous Type I formulation; some of this reduction was due to the removal of nonylphenol ethoxylate surfactant. Some manufacturers have removed tolyltriazole corrosion inhibitors from formulations as well. Many of the improvements followed a change in AMS 1424 standards, which now include a numerical minimum of 4,000 mg/L for Type I formulations. Several Type I products now have acute toxicity levels greater than 10,000 mg/L for tested aquatic organisms, a marked improvement over many previous Type I formulations. Some European communities have developed restrictions on deicer additives, forcing a removal of additives such as triazoles and APE. Manufacturers of some deicer formulations sold in the United States also appear to be in the process of removing triazoles and APE.

Four manufacturers introduced new Type IV formulations for the 2007–2008 winter season with assertions that these formulations were more environmentally friendly than past AAF formulations. These formulations have yet to be studied through independent research.

The acetate- and formate-based pavement deicers and anti-icers used today are typically much less toxic than the urea-based products of the past, which resulted in very high ammonia concentrations in runoff. In addition, the acetate- and formate-based products have significantly improved BOD characteristics as compared to urea and glycols.

Knowledge and Data Gaps

- The most current information on BOD and toxicity of new and developing formulations
- Threshold constituent concentrations for the control of bacterial growths
- Threshold constituent concentrations for the control of objectionable odors
- Standardized testing and reporting methods in manufacturer literature
- Identification of additives in current deicer formulations that are responsible for toxicity
- Characterization of BOD and COD in deicers for different temperatures and salinity
- Verification of toxicity source in pavement deicer and anti-icing formulations
- Identification of unique tracers to help determine which formulations are present in airport runoff
- Monitoring data for additives in airport runoff to represent a broad range of geographically diverse airport situations
- Fate and transport characteristics of ADF and AAF additives, including degradation pathways
- Environmental impact, fate, and transport of pavement deicers

- Monitoring data for FPDs of pavement deicers and anti-icers to represent a broad range of geographically diverse airport situations

Characteristics of Deicers in Wastewater Treatment Systems

For the purposes of this investigation, the treatability of deicer runoff is influenced by the organic constituents' biodegradability and toxicity. These two characteristics determine the basic types of treatment that can potentially be applied. If the constituents are subject to biodegradation, then biological processes have potential applicability. If they are not, then only physical/chemical processes can be used.

As described above, the organic components in deicing fluids include FPDs as well as various categories of additives. The most commonly used FPDs (i.e., PG, EG, acetate, and formate) are all readily biodegradable under both aerobic and anaerobic methanogenic conditions (Switzenbaum et al., 2001). Biodegradation of urea, a runway FPD, occurs readily under aerobic conditions but releases ammonia, which is toxic to aquatic organisms at higher concentrations. Although there are concerns about the impacts of EG on higher life forms (i.e., mammals), it does not exhibit significant toxicity to microorganisms, macroinvertebrates, and fish at the concentrations found in deicer runoff. Thus, because of the ease with which the FPDs can be biodegraded, their primary impact on biological treatment systems is increased load.

Nonionic surfactants, including NPEs, have been found in deicer wastewaters (Corsi et al., 2003). There has been considerable evidence that NP is a degradation product of NPE surfactants and that it accumulates in the environment (Corvini et al., 2006; Ferguson et al., 2003; Ying et al., 2002). One study suggested that its formation is favored in anaerobic digesters (Giger et al., 1984) although a more recent study (Chang et al., 2005) has indicated its degradation there. The difference may be due to the potential isomers of NP and their different susceptibilities to biodegradation (Corvini et al., 2006). Recent research suggests that NP can be degraded aerobically by both bacteria and fungi (Corvini et al., 2006) under appropriate conditions and that NPE can be mineralized by bacterial cultures without the accumulation of metabolites (Naylor et al., 2006). However, because of the uncertainties surrounding the biodegradation of NPEs, their fate in treatment systems for deicer runoff is also uncertain. Furthermore, their presence in sludge undergoing anaerobic digestion can impact the toxicity of benzotriazole corrosion inhibitors, depending on the surfactant concentration (Gruden and Hernandez, 2002).

The only corrosion inhibitors identified in deicers are benzotriazole and tolyltriazoles (4- and 5-methyl benzotriazole) (Cancilla et al., 1997). Benzotriazoles are one of the toxic components in deicers and are resistant to biodegradation (Castro et al., 2005). They have been shown to inhibit methanogenic activity of anaerobic biomass (Gruden and Hernandez, 2002) as well as aerobic subsurface biodegradation of acetate, formate, glycol, and toluene (Jia et al., 2006). In addition, Cornell et al. (2000) found that 5-methyl benzotriazole inhibited the aerobic degradation of PG. Given their characteristics, the benzotriazoles are unlikely to be biodegraded in typical biological treatment systems (Castro et al., 2005), and they have been found in the effluents from wastewater treatment plants (Giger et al., 2006; Weiss et al., 2006). Furthermore, some of the quantity entering an aerobic biological treatment system will be sorbed to the biomass and end up in the sludge disposal system, which could serve as a route to the environment (Gruden and Hernandez, 2002). Weiss et al. (2006) established that treatment using membrane bioreactors was more effective than conventional activated sludge, and that all three forms of benzotriazole were completely mineralized through ozonation. Castro et al. (2005) have demonstrated that plants can perform primary degradation of benzotriazoles, although the transformation products and specific mechanisms were not identified. Nevertheless, the results were encouraging enough for them to propose phytoremediation as a possible treatment technique for removing benzotriazoles from deicer runoff.

Knowledge and Data Gaps

- Fate of surfactants in treatment systems for deicer runoff
- Comparative efficacy of different types of treatment systems with respect to the removal of surfactants and benzotriazoles
- Information on the production of degradation products from the various deicer components by various types of treatment systems

Operational and Infrastructure Considerations

A number of operational and infrastructure impacts on airfield and aircraft have been reported, mostly in association with airfield pavement deicers. In addition to this summary, the recent ACRP 10-03 synthesis project provides comprehensive coverage of this topic.

Pavement Deterioration

Reports have suggested a link between runway surface deterioration and a change in pavement deicers from urea to potassium acetate. In the early 1990s, several Scandinavian airports reported degradation and disintegration of asphalt pavements and softening and stripping effects on bitumen and asphalt concrete that was traced to the use of potassium acetate and potassium formate (Nilsson, 2003). Airports in North America have reported deterioration of concrete pavement in the form of scaling and surface cracking that was determined to be a result of alkali–silica reactivity (ASR), a chemical reaction in cement (Joel, 2005). FAA issued an engineering brief that addresses the impact of ASR in Portland cement concrete when it is exposed to airfield deicing materials, especially potassium acetate–based deicers (Joel, 2005). Findings from research performed by the Innovative Pavement Research Foundation indicate a link between ASR and alkali acetate and formate deicers, and guidance is provided for testing of aggregate mixtures and their reactivity during new construction of concrete runways (Rangaraju, 2007). Trimbath (2006) reported on "map" cracking on runway surfaces traced to a concrete mix that would not have experienced that type of cracking had it not been exposed to potassium acetate. However, it was also reported that of two adjacent concrete panels on the runway, cracking was observed on one but not the other, in spite of the fact that the panels were installed at the same time, illustrating the complexity of the issue. More recent investigations indicate that use of nonreactive aggregates or use of supplementary cementing materials or admixtures can be used to minimize this issue (Rangaraju, 2007).

Airfield Electrical Systems

Increased failure rates of airfield electrical components have been reported by some airports after changing from urea or glycol-based pavement deicers to potassium acetate. The issue appears to be directly related to the increased conductivity of potassium acetate solutions compared to that of urea and glycols. Although some airports have experienced severe problems with airfield electrical systems, others have made the change to potassium acetate with no apparent impact on the longevity of electrical components. Empirical evidence reviewed for ACRP Synthesis 11-03/Topic S10-03 indicated that many of the observed problems were associated with aging, corroding, or poorly maintained electrical infrastructure, which allowed entry of PDMs (Shi, 2008). Corrective actions and improved products and components have reduced or eliminated these problems. A precautionary note has subsequently been added to SAE AMS 1435 regarding specifications for liquid PDMs.

Cadmium Corrosion

Cadmium-plated electrical connectors in the wheel well of the main landing gear of the Boeing 737 New Generation aircraft were found to significantly corrode when exposed to runway deicing fluids containing potassium formate and potassium acetate (Strauss, 2003). Potassium-based PDMs were in widespread use prior to material changes in the aircraft involved. In 2002, based on Boeing Company Service Bulletin 737-24A1148, Transport Canada Civil Aviation issued Aerodrome Safety Circular ASC 2002-015 recommending that airport operators should refrain from using deicing fluids that contain potassium formate on airside movement areas until further notice (Transport Canada, 2002). FAA issued Airworthiness Directive (AD) 2002-16-03 on July 29, 2002, which required "either determining exposure to runway deicing fluids containing potassium formate or performing repetitive inspections of certain electrical connectors in the wheel well of the main landing gear for corrosion" (FAA, 2002).

FAA's AD 2002-16-03 was superseded by AD 2005-18-23, which extends runway deicing fluids to include potassium acetate and extends corrective actions to include cleaning the line replaceable unit (LRU) and applying corrosion-inhibiting compound (CIC) if no corrosion is found, and replacing the LRU with a new LRU in addition to applying CIC if corrosion is found (FAA, 2005). In 2004, the Transport Canada Civil Aviation Safety Circular was cancelled, noting that the problem appeared to be limited to the New Generation series of the Boeing B-737. An Airworthiness Directive was issued, and "airport operators using potassium formate are to notify upon request, air carriers that this deicing fluid is being used at their facilities."

Boeing presented a Boeing 737 New Generation cadmium corrosion update at the spring 2003 SAE G12 meeting detailing their activities in replacing the cadmium-coated safety connectors with anodized aluminum or stainless steel and applying CIC internally and externally to the connectors (Strauss, 2003). At the winter 2006 SAE G12 meeting, Continental Airlines discussed cadmium corrosion problems with their aircraft and the need to develop a new AMS 1435 testing method for cadmium corrosion (Duncan, 2006).

Carbon-Carbon Brake System Oxidation

A 2006 letter from Boeing and Airbus highlighted the problems associated with catalytic oxidation of aircraft carbon brakes (Arriaga and Williams, 2006). The more environmentally advantaged potassium formate– and acetate-based runway deicers were first introduced in Europe in 1988, before the widespread adoption of carbon brakes. In the Boeing and Airbus letter, it was reported that these PDMs appear to promote catalytic oxidation of carbon composite brake components, softening the carbon and possibly leading to brake failure. Application of pavement deicers on runways leads to pavement deicer runoff exposure to the undercarriage and on the brake units in the undercarriage bay and onto or into the carbon disks. In addition, this letter reported that potassium acetate is more aggressive than potassium formate in promoting carbon brake failures. This issue is being actively investigated by a variety of entities, including the SAE G12 committee's Catalytic Oxidation Work Group and an ACRP synthesis project (10-03).

In 1998, the U.S. Air Force evaluated the compatibility of new commercial formulations of runway deicing control products with aerospace materials, many of which are common to both commercial and military aircraft (Gulley, 1998). Deicing materials tested were a glycol mix (Union Carbide), potassium acetate (Cryotech), sodium formate (Old World Industries), sodium acetate (Octagon Process), and urea (People's Moss Gin Co., Inc.). Three brake manufacturers supplied uncoated and antioxidant-coated carbon-carbon material coupons. In carbon-carbon brake systems, nonwear surfaces are the only areas coated with the antioxidant coatings, whereas all wear surfaces, which constitute most of the carbon-carbon brake, are unprotected. The coupons were tested for resistance to oxidation and hardness. The noncoated coupons showed an increased oxidation rate, three to five times higher than the coated coupons when exposed to typical 700°C (1,300°F) temperatures for 8 hours. The deicers containing potassium and sodium had the greatest effect on oxidation, followed closely by the glycol mix; the coupons were least affected by the urea deicer. All of the noncoated carbon-carbon materials had a loss in hardness after being exposed to all the runway deicing materials. Loss in hardness will reduce wear performance capability. Hardness increased on some coated carbon-carbon materials.

Residuals

Residues from Type II and Type IV fluids may form on aerodynamically quiet areas (Kotker, 1998). These residues form when thickened fluids dry out during flight, leaving a powderlike residue on the aircraft surface. If the residue is not removed, either by deicing or anti-icing, it might absorb rainwater (rehydrate) and subsequently freeze, restricting the movement of unpowered flight control surfaces. A cautionary note was added to ARP 4737 (Section 6.3.1.2) to require the removal of these residues.

The METSS ADF-2 and Battelle D3 Type I environmentally advantaged deicing fluids (described in more detail in the "Deicer Products Under Development" section, below) that were demonstrated on U.S. Air Force KC-135 aircraft did not perform acceptably because of fluid thickening on the aircraft surface (METSS ADF-2) and the extensive amounts of residuals in the form of particulates left on the surface of the aircraft (Battelle D3). Because these problems were not noted during AMS 1424 certification of the fluids, it would appear that the application method and the environmental conditions are factors in the residual formation. The neat deicing fluids were mixed with water, heated to about 65°C (150°F), and then sprayed on the aircraft. The METSS ADF contained sorbitol and formate salts. At the mixing temperature, all of the components of the mixture remained in solution. It is suspected that the salts came out of solution as the mixture was sprayed on the aircraft, leaving a thickened fluid on the aircraft surface because of the high evaporation rate of the ADF and the cold surface. Similarly, the Battelle D3 fluid contained glycerol and some higher-molecular-weight sugars, which may have precipitated out on the cold aircraft surface.

Knowledge and Data Gaps

- Strategies to mitigate pavement and airfield-lighting deterioration and catalytic oxidation of aircraft carbon brakes.

Deicer Products under Development

During the past 10 years, there have been a number of efforts to develop deicing and anti-icing fluids that are more environmentally friendly than currently available deicers. The results of these efforts are summarized in the following paragraphs. None of these formulations are currently approved for use, but the information may be useful for defining potential improvements that could be made through this project.

Battelle D3

Battelle Memorial Institute developed a deicing/anti-icing fluid that contains bio-based polyol FPDs (Samuels et al., 2006; Simmons et al., 2007). The deicer/anti-icing fluid has been designated D3: Degradable by Design™. The preferred type of polyol FPD is glycerol. The BOD of D3 is reported to be about one-third of the BOD of PG, and the LD_{50} for fathead minnows was reported to be greater than 10,000 mg/L (Simmons et al., 2007). The D3 fluid was evaluated twice (2006 and 2007) on KC-135 military aircraft by the U.S. Air Force at the Niagara Falls Air Reserve Station (Niagara Falls, N.Y.) under the support of the Environmental Security Technology Certification Program (ESTCP). The D3 fluid used in the first test was modified slightly for the second test. Both fluids were certified under AMS 1424. In both cases, the test results were unfavorable because extensive amounts of the residual fluid in the form of particulate deposits remained on the surface of the aircraft. Unpublished data collected during the second evaluation shows a BOD_5 approximately 86 percent that of a PG-based Type I ADF.

Battelle has also developed a proprietary process with the intention of manufacturing an improved, environmentally advantaged pavement deicing fluid (D3-RDF) based on the use of low-cost, bio-based materials (Chauhan et al., 2006). A byproduct stream is obtained from a process that produces monoalkyl esters of long-chain fatty acids. The byproduct stream includes water, glycerol, and an alkali-containing compound. The stream is converted to a deicing/anti-icing fluid by the addition of an acid to neutralize the alkali-containing compound to produce an alkali salt that functions as a supplemental FPD. As with the D3 aircraft deicing fluid, the primary FPD is glycerol. Presently, Battelle is under contract to the Strategic Environmental Research and Development Program (SERDP) to develop modified D3-RDFs using different chemistries that are less corrosive to aircraft components—including carbon-carbon brakes and cadmium plating—and less expensive than existing PDMs. Preliminary data indicate that some D3-RDFs have lower COD and BOD levels and an order-of-magnitude lower aquatic toxicity than PG–based and organic salt PDMs at comparable freezing points and friction coefficients (Chauhan, 2007).

Foster-Miller Low-BOD Fluid

Under SERDP sponsorship, Foster-Miller (Waltham, Mass.) developed new aircraft deicing and anti-icing fluids with the intention of providing high-performance environmentally advantaged options which can be safely released to the environment without post-treatment (Westmark et al., 2001). The candidate formulations were designed using computer modeling techniques to predict component and mixture properties and were subjected to a series of tests to evaluate deicing/anti-icing performance, compatibility with aircraft materials, environmental impact, and cost. Three prototype formulations were developed and evaluated for use by commercial and military aviation:

- A low-BOD_5 Type I deicer formulation containing two FPDs, water, a non-ionic surfactant, and a corrosion inhibitor
- A biotreatable Type I deicer containing an FPD, water, and a non-ionic surfactant
- A low-BOD_5 Type II anti-icing fluid containing two FPDs, water, a polysaccharide thickener, and a non-ionic surfactant

The FPDs, surfactants, corrosion inhibitor, and thickener were selected for their low aquatic toxicity relative to other materials in the same categories.

The BOD and rate of degradation of the low-BOD_5 Type I fluid can be tailored by adjusting the relative ratios of the two FPDs, allowing for the production of fluids that can be customized to a user's particular environmental setting and needs. A slowly degrading low-BOD_5 Type I aircraft deicing fluid—specifically developed for use where the deicing runoff is discharged into sensitive receiving waters or where airfields may otherwise be forced to build aggressive runoff, capture, containment, and treatment systems—was recently demonstrated by the U.S. Air Force under support by ESTCP. The Type I deicer formulation developed under the SERDP program was modified by adding an antifoaming agent and changing the corrosion inhibitor. The fluid was certified and evaluated on KC-135s at the Niagara Falls Air Reserve Station. The fluid performed well, except for some foaming on the surface of the aircraft. Foster-Miller is presently evaluating alternative nonfoaming surfactants.

METSS Type I

Under the support of the U.S. Air Force, METSS (Westerville, Ohio) developed a non-glycol-based deicing/anti-icing fluid, METSS ADF. This fluid was designed as an environmentally friendly (i.e., nontoxic and nonhazardous to plant and animal life) drop-in replacement for PG- and EG-based fluids to reduce the requirement for capturing or treating the fluid prior to its release into the environment. METSS ADF is based on a combination of glucose, lactates, and their salts (Sapienza, 2003, 2005). The components are derived from renewable agricultural products and are 100 percent organic.

METSS ADF-2 is a slightly different formulation of the early METSS ADF and contains sorbitol and formate salts. Product literature indicates a BOD_5 of approximately 350,000 mg/L, approximately 60 percent of that of PG (METSS Corporation, 2002). The literature also provides aquatic toxicity data, with a 48-hour LC_{50} for *Daphnia magna* of 14,375 mg/L, and a 96-hour LC_{50} for *Pimephales promelas* of 12,275 mg/L.

The U.S. Air Force evaluated METSS ADF-2 on KC-135R aircraft at the Niagara Falls Air Reserve Station. Prior to field testing, the fluid was tested and certified in accordance with AMS 1424D, Deicing/Anti-icing Fluid, Aircraft Type I The field results were unfavorable because the fluid thickened on the aircraft surface shortly after (within approximately 5 min of) its application and did not migrate like the typical PG-based fluids. (Van Scoyoc, 2004). The fluid was subsequently removed from the list of FAA-qualified fluids for 2004–2005.

Knowledge and Data Gaps

- Status of commercialization of newly developed fluids

Methodological Issues

Several potentially relevant methodological issues were identified in the literature and are summarized in the following subsections.

BOD Analysis

The standard BOD analysis is a 5-day bioassay technique (BOD_5) that requires five key components: a food (carbon) source, microorganisms, oxygen, the appropriate temperature, and a source of nutrients to provide optimal growth for organisms. If any of these components is missing or inadequate, the test cannot be performed satisfactorily. Temperature and nutrient levels are operationally controlled in the BOD testing process. However, microorganism and carbon levels are sample dependent and are problematic, particularly in the analysis of deicers.

Typical laboratory techniques for BOD_5 follow method 5210B in *Standard Methods for the Examination of Water and Wastewater* (APHA, 1995). BOD analysis of environmental samples containing deicer or pure deicer formulations is particularly challenging because of the limitations of the test and the considerable oxygen demand these materials can have during the test period. Oxygen demand in environmental samples containing deicer is difficult to predict, and only a limited amount of oxygen is available to drive the reaction. Frequently, laboratories tend to overdilute or underdilute (too little or too much food, respectively) the sample when the test is performed. The analyst will not know whether the sample was prepared properly until 5 days later, at the conclusion of the test.

Microorganism population can be limiting when dealing with the BOD analysis of deicers. Experience performing 40-day BOD analysis has shown a significant lag in oxygen demand caused by either the inadequate number of microorganisms at the beginning of the test or the inability of organisms to adapt to the deicers as a food source. Over the last 12 years the Wisconsin State Laboratory of Hygiene has developed strategies to deal with the limitations of the BOD test in dealing with deicers, including initial screening and modifications to the standard test protocols.

The COD test provides results within hours and is used as a predictor of the BOD level in both environmental samples containing deicer and pure deicer formulations. COD results from environmental samples have been correlated to BOD_5 concentrations to provide a screening level estimate of BOD magnitude, information that can be used to prepare appropriately diluted deicer samples for BOD testing.

Further complication in transferring laboratory-generated BOD information to an environmental situation occurs because of the differences in environmental conditions between airport runoff and laboratory conditions of standard BOD_5 tests. Deicing and anti-icing activities occur typically during periods of colder temperatures and over longer periods of time than that do standard testing procedures; typically, microorganism populations are different too. Laboratory conditions cannot be expected to simulate environmental conditions exactly; however, low-temperature tests, longer-duration tests, and tests using microorganisms that are acclimated to deicer exposure are possible modifications to standard laboratory testing procedures that can make BOD results more useful in interpreting monitoring data and predicting environmental BOD exertion. In addition, using a BOD bottle larger than the traditional 300-mL bottle provides greater flexibility and reduces error introduced by serial dilutions.

Benzotriazoles Analysis

Several types of benzotriazoles—including 1H-benzotrizaole (CAS #95-14-7) and isomers 4-methyl-1H-benzotriazole and 5-methyl-1H-benzotriazole (CAS #136-85-6)—are commonly added to deicers as corrosion inhibitors,. Various abbreviations have been used for these compounds in the literature: 1H-benzotriazole has been referred to as BT, 1H-BT, BTri, BTAH, BTA, BZT, and Bz. The 4- and 5-methyl-1H-benzotriazole isomers are commonly known as tolyltriazole, which has been abbreviated TT, TTri, MBT, MeBTA, or MBz. Individually, these compounds have been abbreviated as 4- and 5-MeBT, 4- and 5-TTri, or 4- and 5-TT. The structure of benzotriazole was determined as early as 1896 (Fieser and Ames, 1927), and synthesis reactions were published as early as 1921 (Charrier and Beretta, 1921). In the 1960s, benzotriazole was identified as a corrosion inhibitor for copper (Cotton and Scholes, 1967).

Various methods of extraction and instrumental analysis have been used to detect triazoles in environmental samples and lab-prepared solutions (Table 2-14). Ultraviolet (UV) absorbance was first used in the 1950s to determine the UV spectra of benzotriazole molecules (Fagel and Ewing, 1951). Gas chromatography coupled with mass spectrometry (GC/MS) has been the most commonly used method of analysis in recent years, with detection limits ranging from 0.1 µg/L to 0.08 mg/L (Breedveld et al., 2003; Cancilla, 1998; Corsi et al., 2003). Gas chromatography with a flame ionization detector (GC/FID) can also be used to verify the presence of triazoles (Cancilla, 1998; Corsi et al., 2006a). High-pressure liquid chromatography with a UV detector (HPLC-UV) has been used to measure triazole concentrations, with detection limits ranging from 0.5 to 1.0 ppm (Castro, Davis, and Erickson, 2004; Cornell et al., 2000; Gruden, Dow, and Hernandez, 2001; Pillard et al., 2001). UV-visible spectrophotometry (UV-VIS) has recently been used to determine triazole concentrations in soil extracts, with a detection limit of 0.1 mg/L for both BT and TT (Jia et al., 2007).

TABLE 2-14 Examples of Recent Triazole Extraction and Analysis Methods

Reference	Matrix	Extraction	Analysis
Cancilla, 1998	water	liquid/liquid	GC/MS
Cornell et al., 2000	water	—	HPLC-UV

TABLE 2-14 Examples of Recent Triazole Extraction and Analysis Methods

Reference	Matrix	Extraction	Analysis
Gruden et al., 2001	wastewater sludge	none	HPLC-UV
Pillard et al., 2001	water	—	HPLC-UV
Kolpin et al., 2002	water	liquid/liquid	GC/MS
Cancilla et al., 2003a	water	SPE	GC/MS
	fish	liquid/liquid	GC/MS
Cancilla et al. 2003b	water	SPE	GC/MS
	soil	SPE	GC/MS
Corsi et al., 2003	water	SPE	GC/MS
Breedveld et al., 2003	water	SPE	GC/MS
	soil	—	LC/MS
Castro et al., 2004	water	—	HPLC-UV
Hart et al., 2004	soil solution	—	HPLC-UV
Weiss and Reemtsma, 2005	water	none/SPE	LC/MS
Corsi et al., 2006b	water	SPE	GC/MS
Corsi et al., 2006a	deicers	—	GC/FID
Giger et al., 2006	water	SPE	LC/MS
Reemtsma et al., 2006	water	—	LC/MS
Weiss et al., 2006	water	none	LC/MS
Jia et al., 2007	soil	—	UV-VIS

Recently, the use of liquid chromatography–tandem mass spectrometry (LC/MS/MS) has become the preferred method for the analysis of triazoles, with limits of detection for water samples as low as 8 ng/L BT and 3 ng/L TT, and for soil extracts 0.1 mg/kg BT (Breedveld et al., 2003; Giger et al., 2006). Calculated limits of detection for both BT and TT in water samples have also been reported as 33 ng/L (Weiss and Reemtsma, 2005). While LC/MS/MS has the potential to be widely used for triazole analysis, published studies have used different instrumental methods to determine triazole concentrations (Giger et al., 2006; Weiss and Reemtsma, 2005). There are numerous LC/MS/MS parameters, and slight changes can result in different detection limits, elution times, and peak separation between the 4- and 5-MeBT isomers. Further method development and analysis using LC/MS/MS will allow triazole concentrations in environmental samples to be more accurately reported.

Although triazoles have been analyzed in surface water and groundwater samples from airports, few studies have attempted to determine triazole concentrations in environmental soil samples, and those that have used different methods of extraction and analysis. For example, Cancilla et al. (2003a) used methylene chloride to extract soil samples for GC/MS analysis, whereas Breedveld et al. (2003) used methanol for soil extraction, which was diluted with water before being analyzed with LC/MS/MS. In an attempt to explain the movement of triazoles in the environment, soil sorption studies have been performed by adding a range of triazole concentrations to different soil types in the United States and Europe (Hart et al., 2004; Jia et al., 2007). Additional soil studies and the development of efficient extraction methods will clarify the fate and transport model for triazoles.

Alkylphenol Ethoxylates Analysis

APEs are components of some deicer formulations and, as stated previously, these nonionic surfactants can be problematic because of their contribution to aquatic toxicity. The two most commonly used APE formulations are nonylphenol ethoxylate (CAS #9016-45-9) and octylphenol ethoxylate (CAS #9036-19-5) surfactants. The United States, the European Union, and Canada have all conducted environmental risk assessments of NPE, the most prevalent APE, or its most common breakdown product, nonylphenol (Environment Canada and Health Canada, 2001; European Commission, 2000). In the United States, NP is regulated by EPA via ambient aquatic life water quality criteria (EPA, 2005). The occurrence of APE, including NP, in deicer formulations and deicing runoff is therefore of concern.

Numerous analytical methods for determining APE in complex media have been developed over the years, using techniques including GC/MS, HPLC, and LC/MS (Table 2-15). Significant challenges exist for high-performance detection and quantitation of APEs in deicer-derived samples. APEs typically are formulated as a complex mixture of molecular species having a distribution of ethoxyl-chain lengths and alkyl-chain isomers. Of paramount concern in any analytical method to be used for APE analysis in deicer-derived samples is determination of the ethoxyl-chain length distribution of the formulation. This parameter will determine factors such as solubility and phase-partitioning (Ahel and Giger, 1993a, 1993b), toxicity (Servos, 1999), and fate and transport (Ferguson and Brownawell, 2003; Ferguson et al., 2003; Jonkers et al., 2001, 2003) of APE in the environment. Therefore, the most suitable methods for use in deicer-derived APE analysis are those that provide the capability to discriminate EOs of APE. In particular, the combination of either normal-phase or size-exclusion chromatography with electrospray mass spectrometry provides highly selective EO-discriminating analysis of APE in environmental extracts (Ferguson et al., 2001; Loyo-Rosales et al., 2003; Shang et al., 1999). Among these methods, the size-exclusion LC/MS methods are the most robust and useful for analysis of APE in complex deicer-derived samples. This is due primarily to their combination with isotopically labeled surrogate standards for quantitation and their facile combination with aqueous-based sample preparation methods (e.g., solid-phase extraction). They are quite sensitive, with detection limits in the low nanogram-per-liter range (more than sufficient for analysis of most deicers, deicing runoff, and receiving waters). In addition, these methods suffer much less from matrix-induced ionization suppression, which can be a problem with analysis of APE in complex samples such as wastewater or sediment when using electrospray mass spectrometry detection (Ferguson et al., 2000).

TABLE 2-15 Examples of Recent APE Analysis Methods

Reference	Matrix	Extraction	Analysis
Giger et al., 1981	wastewater	liquid/liquid	GC/MS

TABLE 2-15 Examples of Recent APE Analysis Methods

Reference	Matrix	Extraction	Analysis
Ding and Tzing, 1998	water	SPE	GC/MS
	wastewater		
Marcomini and Giger, 1987	sediment sludge	soxhlet	HPLC-fluorescence
Scarlett et al., 1994	wastewater	gas-stripping	HPLC-UV
de Voogt et al., 1997	sediment	soxhlet	GC/MS
	sludge		HPLC-UV
Ding and Tzing, 1998	wastewater	gas-stripping	HPLC-UV
Ahel et al., 2000	wastewater	liquid/liquid	HPLC-fluorescence
Crescenzi et al., 1995	water	SPE	HPLC-MS
	wastewater		
Shang et al., 1999	sediment	soxhlet	HPLC-MS
Ferguson et al., 2000	water	SPE	HPLC-MS
	sediment	sonication	
Ferguson et al., 2001	wastewater	SPE	HPLC-MS
	sediment	sonication	
Loyo-Rosales et al., 2003	water	SPE	HPLC-MS/MS
	sediment	soxhlet	

Previous work on APE occurrence in deicers and impacted environmental samples (e.g., runoff and snow banks at airports) (Corsi et al., 2003, 2006b) has been conducted using the abovementioned size-exclusion LC/MS methods, resulting in highly definitive reports of the presence of these compounds and their degradation products. It is expected that future work in this area will continue to use these specific methods when conducting detailed studies on fate and transport of deicer-derived APEs and their degradation products in aqueous environments.

Current challenges for APE analysis in deicer formulations and environmental samples include development of rapid assessment methods for determining the presence and concentration of these compounds. The LC/MS methods described above are labor intensive and difficult to automate. Current work is being focused on use of alternative mass spectrometric methods (e.g., matrix-assisted laser desorption/ionization) that will simplify sample preparation and allow very fast APE identification and measurement in a variety of sample types, including deicers and environmental samples.

Toxicity Test Methods

Airport deicing discharges are regulated under the Clean Water Act through permits issued under the National Pollutant Discharge Elimination System (NPDES). Permits may require discharge monitoring for deicer-related parameters such as BOD, glycols, metals, ammonia-nitrogen, and pH. Where impacts of deicer toxicity on aquatic life are a concern, aquatic toxicity tests may be required for permit compliance.

In 1999, the Air Transport Association recommended that the SAE begin requiring deicer formulators to test new products using species that have been selected by regulatory agencies for inclusion in discharge permits. The species and test conditions are specified in EPA guidelines for acute and chronic whole effluent testing manuals (EPA Office of Water, 2002; EPA, 2002). Freshwater species required by most states include the fathead minnow (*Pimephales promelas*) and the daphnid *Ceriodaphnia dubia*. Estuarine and marine test organisms include the inland silverside (*Menidia beryllina*), sheepshead minnow (*Cyprinodon variegatus*), and the mysid (*Mysidopsis bahia*).

Although toxicity tests performed in a laboratory under controlled conditions of light and temperature provide valuable ecological information, laboratory conditions do not mimic actual conditions. This is especially true for deicer runoff from airports during winter conditions when temperatures are typically well below laboratory test conditions. Bacterial metabolism is reduced with low water temperatures, and a laboratory BOD test under standard conditions is not a very good predictor of in situ BOD exertion and DO levels during deicing conditions (Corsi et al., 2001a). Toxicity test results, however, do not seem to be dramatically affected by temperature. Corsi et al., 2001b) found that LCs were not substantially changed under colder test conditions. In tests of one deicer, *C. dubia* were slightly less sensitive in tests performed at 6°C, whereas fathead minnow were slightly more sensitive in tests performed at 10°C (standard acute test temperature 20°C)

Because the glycols typically used in deicers have very high BODs, one potential problem when conducting toxicity tests of airport runoff is maintaining adequate levels. Low oxygen levels can lead to mortality indirectly related to glycols in deicers. EPA recommends aerating a test when DO levels fall below 4.0 mg/L (for warm water species). Low DO is a common problem when conducting the fathead minnow chronic test on airport runoff samples. This problem is likely enhanced by the brine shrimp (*Artemia sp.*) added as food for the fish. Any uneaten brine shrimp can serve as a food source for bacteria in the water (i.e., an additional source of BOD), resulting in reductions in DO in the test chamber that are unrelated to deicer content. One way to reduce the risk of low-DO levels in the fathead minnow chronic test is to reduce the number of fish per replicate and reduce the sample volume. Reducing sample volume increases the surface area, which facilitates gas exchange and improves DO levels during the tests (Geis et al., 2003). This method modification provides an improved assessment of toxicity due to deicer additives, which can otherwise be masked by mortality due to glycol-associated BOD.

Operational Characteristics Testing

In the United States, deicing/anti-icing fluids used on commercial and military aircraft are developed and manufactured to industry standards and published by SAE. Similar standards are also published by the Association of European Airlines and ISO. The SAE

AMS standards relating to aircraft and runway deicing and anti-icing fluids and runway solids are given in Table 2-16.

TABLE 2-16 Standards for Aircraft and Runway Deicing/Anti-icing Fluids and Runway Solids

Document	Revision	Publication Date	Document Title
AMS 1424	H	July 2007	Deicing/Anti-Icing Fluid, Aircraft, SAE Type I
AMS 1425	C	January 1995	Deicing Fluid, Aircraft, Ethylene Glycol Base
AMS 1426	C	October 1993	Fluid, Deicing/Anti-Icing, Runways and Taxiways Glycol Base
AMS 1427	A	January 1995	Deicing/Anti-Icing Fluid, Aircraft, Propylene-Glycol Base
AMS 1428	F	July 2007	Fluid, Aircraft Deicing/Anti-Icing, Non-Newtonian (Pseudoplastic), SAE Types II, III and IV
AMS 1431	B	August 1998	Compound, Solid Runway and Taxiway Deicing/Anti-Icing
AMS 1435	A	August 1999	Fluid, Generic, Deicing/Anti-Icing Runways and Taxiways
ARP 4737	G	November 2005	Aircraft Deicing/Anti-Icing Methods

Table 2-17 summarizes AMS requirements for aircraft and runway deicing/anti-icing liquids. Standards referencing some of the requirements are also shown in Table 2-16. These standards can be obtained from SAE International (Warrendale, Pa.), *Annual Book of ASTM Standards: Water and Environmental Technology* (American Society for Testing and Materials [ASTM], 1993), and *Standard Methods for the Examination of Water and Waste Water* from the American Public Health Association (APHA).

TABLE 2-17 AMS Requirements for the Most Common Aircraft and Runway Deicing/Anti-icing Liquids

	AMS			
	1424H	1428F	1431B	1435A
Scope				
Form	X	X	X	X
Application	X	X	X	X
Precautions	X	X	X	X
Safety—hazardous materials	X	X	X	X
Technical Requirements				
Material	X	X	X	X
Non-glycol-based fluids	X	X	X	—
Appearance	X	X	X	X
Toxicity	X	X	—	—
Environmental information (APHA)	X	X	X	X
BOD	X	X	X	X
TOD or COD	X	X	X	X
Biodegradability	X	X	X	X
Aquatic Toxicity	X	X	X	X

TABLE 2-17 AMS Requirements for the Most Common Aircraft and Runway Deicing/Anti-icing Liquids

	AMS			
	1424H	**1428F**	**1431B**	**1435A**
Trace Contaminants	X	X	X	X
Phase Diagram	—	—	X	—
Chemical Analysis	—	—	X	—
Physical Properties (APHA)				
Flash Point (ASTM D93, D3278)	X	X	X	X
Specific Gravity (ASTM D891)	X	X		X
pH (ASTM E70)	X	X	X	X
Chloride Content	—	—	X	
Refractive Index (ASTM D1747)	X	X	—	—
Freezing Point (ASTM D1177)	X	—	—	X
Surface Tension	X	X	—	—
Viscosity (ASTM D445)	X	—	—	—
Fluid Stability	—	—	—	—
Storage Stability (ASTM F1104)	X	X	X	X
Thermal Stability	X	X	—	—
Thin Film Thermal Stability		X	—	—
Hard Water Stability	X	X	—	—
Shear Stability	X	X	—	—
Exposure to Dry Air	—	X	—	—
Tendency to Foam	—	X	—	—
Cold Storage Stability	—	X	—	—
Rheological Properties				
Viscosity	—	X	—	—
Effect on Aircraft Materials				
Sandwich Corrosion (ASTM F1110)	X	X	X	X
Total Immersion Corrosion (ASTM F483)	X	X	X	X
Low Embrittling Cadmium Plate (ASTM F111)	X	X	X	X
Stress-Corrosion Resistance (ASTM F945)	X	X	X	X
Hydrogen Embrittlement (ASTM F519)	X	X	X	X
Effect on Transparent Plastics (ASTM F484)	X	X	X	X
Effect on Painted Surfaces (ASTM F502)	X	X	X	X
Effect on Unpainted Surfaces (ASTM F485)	X	X	X	X
Runway Concrete Scaling Resistance (ASTM C672)	X	X	X	X
Rinsability	—	—	—	X
Performance Properties	—	—	—	X
Freezing Point (ASTM D1177)	X	X	—	—
Anti-Icing Performance (AS 5901)	X	X	—	—
Aerodynamic Acceptance Test (AS 5900)	X	X	—	—
Remove accumulated frozen deposits of frost and ice from aircraft maneuvering areas	—	—	X	—
Quality Assurance Provisions				

TABLE 2-17 AMS Requirements for the Most Common Aircraft and Runway Deicing/Anti-icing Liquids

	AMS			
	1424H	**1428F**	**1431B**	**1435A**
Responsibility for Inspection	X	X	X	X
Classification of Tests	X	X	X	X
Acceptance Tests	X	X	X	X
Periodic Tests	X	X	X	X
Preproduction Tests	X	X	X	X
Sampling and Testing	X	X	X	X
Bulk Shipments (ASTM D4177)	X	X	—	X
Drum Shipments (ASTM D1568)	X	X	—	X
Acceptance Tests	X	—	—	—
Preproduction and Periodic Tests	X	—	—	—
Statistical Sampling Plan	X	X	X	—
Approval	X	X	X	X
Reports	X	X	X	X
Resampling and Retesting	X	X	X	X
Preparation for Delivery				
Packaging and Identification	X	X	X	X
Acknowledgement	X	X	X	X
Rejections	X	X	X	X
Similar Specifications	X	X	—	—
Notes	X	X	X	X

Under FAA regulations, takeoff is prohibited if any contamination by winter precipitation (frost, ice, or snow) adheres to the airplane wings, propellers, or control surfaces. Takeoff is also prohibited any time that contamination due to winter precipitation can be expected to adhere to the aircraft, based on holdover time timetables approved by the FAA and Transport Canada. Holdover time is the time from when deicing or anti-icing fluid is applied to when contamination by winter precipitation begins to accumulate or re-adhere to a surface. The SAE standards do not include performance specifications for holdover times but instead contain two requirements for anti-icing performance, namely a water spray endurance test and a high-humidity endurance test. Holdover time guidelines are published in SAE ARP 4737; this standard does not include performance specifications for determining holdover time guidelines. Holdover time guidelines for each deicing/anti-icing fluid are determined annually in test programs funded by the FAA and Transport Canada.

SECTION 3

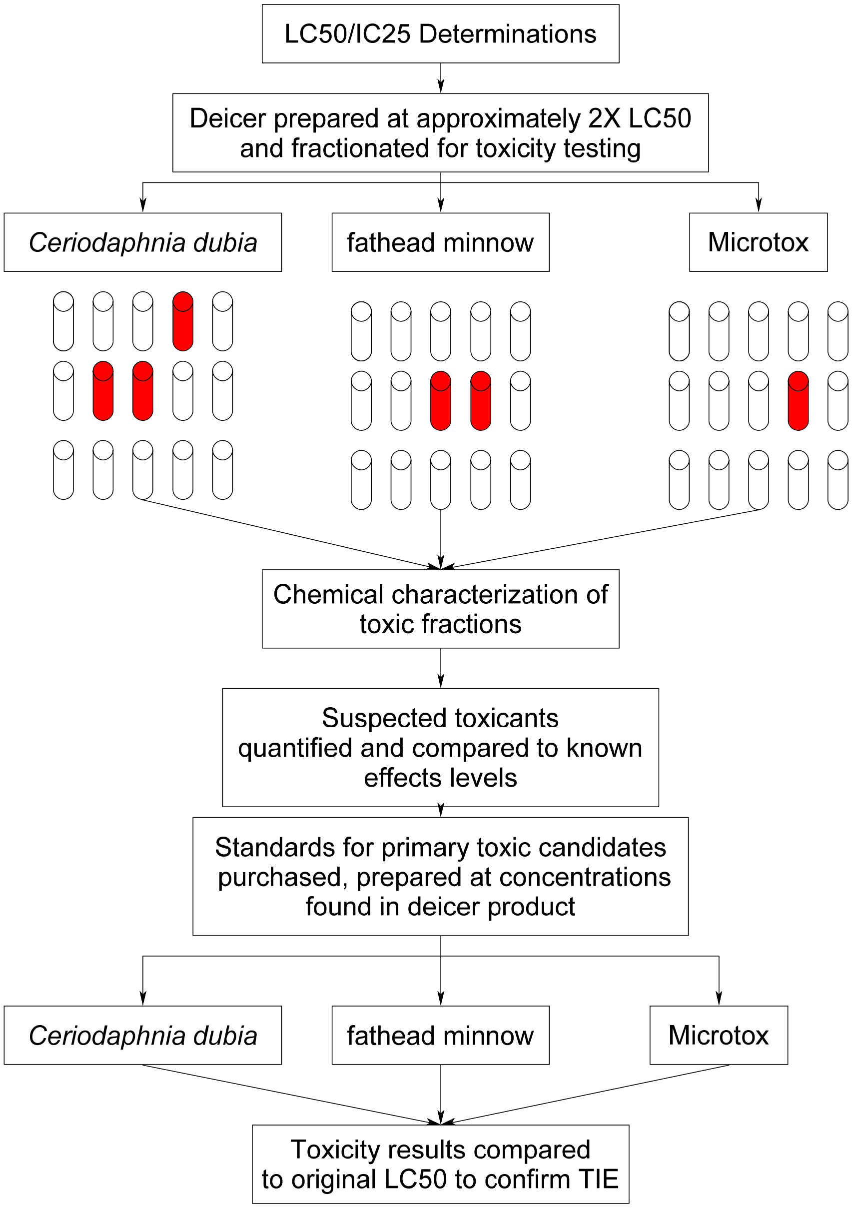
AIRCRAFT AND AIRFIELD DEICING FORMULATIONS COMPONENTS ASSESSMENT

Laboratory analyses were conducted to characterize two critical aspects of currently used deicers: aquatic toxicity and BOD. This section describes the analytical methods employed and the results of those analyses.

Toxicity Assessment

The specific aim of the toxicity assessment was to identify as clearly as possible the chemical components of selected commercial deicer formulations that contribute most to aquatic toxicity. This was accomplished using an approach known as toxicity identification and evaluation (TIE, summarized in Figure 3-1). In TIE, chemical fractionation methods were used to separate deicer components prior to toxicity testing of each individual fraction. Fractions that were found to exhibit significant toxicity were then flagged for chemical analysis to identify (and where possible to quantify) the major components present in these isolated fractions. Subsequent work included verification of the toxicity of identified components by toxicity assays of authentic chemical standards where possible as well as targeted quantitative analysis of the chemical classes identified to be of primary concern in the deicer formulation.

Figure 3-1. Scheme for conducting toxicity identification and evaluation assays on deicer products.



Methods

Baseline Toxicity Testing Before beginning work on the TIE process, a total of 14 deicer products (Table 3-1) were screened for toxicity using Microtox and common aquatic regulatory species, including the fathead minnow (*Pimephales promelas*) and the water flea (*Ceriodaphnia dubia*). Twelve of these products, representing the three categories of deicers, were selected for definitive toxicity testing and toxicity identification analysis: Type I aircraft deicers (A, B, C, D, and E), Type IV aircraft anti-icers (H, I, J, and K), and pavement deicers/anti-icers (L, M, and N). Two Type I products were eliminated from the analyses because they are not widely used in the U.S. market. Definitive toxicity tests were conducted following EPA guidelines. Briefly, each definitive acute test consisted of a 50 percent dilution series with five treatments plus a laboratory control. Moderately hard reconstituted water was used as the laboratory control and product dilution water. Each treatment consisted of four replicates with five *C. dubia* or 10 fathead minnow per replicate. The acute assays were conducted in an environmental chamber at 20°C with a 16-hour/8-hour light/dark cycle. Test treatments were renewed daily with freshly prepared solutions, and water quality parameters—including DO, pH, and conductivity—were monitored daily. At 48 hours for *C. dubia* and 96 hours for fathead minnow, the survival per replicate was recorded for calculation of an LC_{50} using Probit or Spearman-Karber analysis, as appropriate.

TABLE 3-1 Summary of Deicer Product Candidates Considered for Inclusion in Toxicity Assays and TIE

Product	Product Type	Freezing Point Depressant
A	Type I Deicer	PG
B	Type I Deicer	EG
C	Type I Deicer	PG
D	Type I Deicer	PG
E	Type I Deicer	PG
F	Type I Deicer	EG
G	Type I Deicer	EG
H	Type IV Anti-Icer	PG
I	Type IV Anti-Icer	EG
J	Type IV Anti-Icer	PG
K	Type IV Anti-Icer	PG
L	Pavement Deicer/Anti-Icer	Potassium Acetate
M	Pavement Deicer/Anti-Icer	Sodium Acetate
N	Pavement Deicer/Anti-Icer	Sodium Formate

Additional range-finding toxicity tests were conducted to evaluate products prior to selection for full toxicity characterization to ensure that the selected products represented a range of toxicity. Range-finding acute assays differed from definitive tests in that fewer replicates and test organisms were used, test solutions were not renewed, and water quality parameters were not monitored.

One deicer product from each category was selected for acute marine toxicity testing using the marine species mysid shrimp (*Mysidopsis bahia*) and inland silverside minnow (*Menidia beryllina*) (Aquatic Research Organisms, Hampton, N.H.). Test conditions were identical to the acute definitive tests described above except for the dilution water and test duration. Laboratory control and product dilution water were prepared at 31 g/L salinity using Crystal Sea (Aquatic Ecosystems, Apopka, Fla.). Test duration for both species was 48 hours.

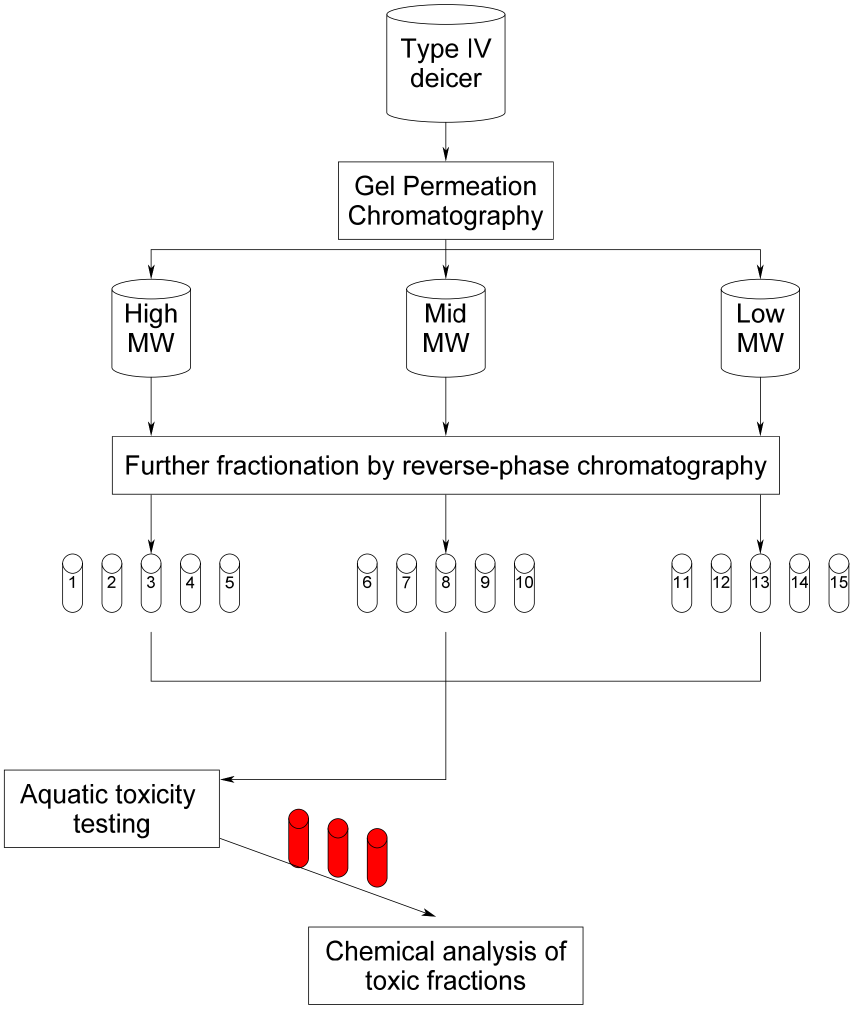
Chronic toxicity tests were performed on all deicer products selected for full toxicity characterization. Chronic tests were used to evaluate sublethal endpoints with fathead minnow (weight) and *C. dubia* (young produced). As was the case with the definitive acute tests, chronic assays consisted of a 50 percent dilution series of five treatments and a laboratory control. Laboratory control and dilution water were moderately hard water. Each treatment was replicated 10 times with one *C. dubia* or two fish per replicate. Organisms were less than 24 hours old at the start of the tests. Tests were maintained in an environmental chamber at 25°C with a 16-hour/8-hour light/dark cycle. Treatments were renewed with freshly prepared solutions daily. Water quality parameters were monitored daily. The number of young in the *C. dubia* test replicates were recorded and removed daily. The *C. dubia* chronic tests were terminated when at least 80 percent of lab control individuals released their third brood (day 6 or 7). The fathead minnow chronic tests were terminated on day 7, when the fish from each replicate were removed for weighing. Three-brood totals and fish dry weight were used to calculate inhibition concentrations (IC_{25}) using the EPA IC_p program.

In addition to the species used in regulatory requirements, the luminescent marine bacterium *Vibrio fischeri*, also known as Microtox®, was included in the battery of toxicity test species. While not used as a regulatory tool, the rapid results can be very useful, especially when evaluating many treatments during toxicity characterization. In this assay, freeze-dried bacteria were rehydrated in a saline solution. A measured aliquot of rehydrated bacteria were added to the test treatments and controls. The luminescence endpoint was determined spectrophotometrically after 15 minutes at a test temperature of 15°C. Effect concentrations (EC_{50}) were calculated using the Microtox software.

Fractionation Methods The overall objective of the fractionation methods outlined below was to separate the chemical components of deicer formulations so that individual components (or, more realistically, simplified mixtures of components) could be assayed for toxicity in isolation. This approach is one third of the (TIE) protocol used in the present study to identify components of deicers contributing to aquatic toxicity. The other two components of this protocol are toxicity testing of the fractions and analytical characterization of the toxic fractions.

Fractionation of Type IV Deicer: Gel Permeation Chromatography and HPLC A two-dimensional chromatographic separation method was applied in order to fractionate the Type IV deicers for further toxicity testing and chemical analysis (Figure 3-2). First, to prepare the Type IV fluid samples for chromatographic fractionation, the polymeric thickener in the fluid was removed by precipitation in tetrahydrofuran (THF). For each of the four Type IV deicers investigated, 100 µL of deicer was mixed with 900 µL of THF in 1.5-mL Teflon microcentrifuge tubes. The tubes were mixed on a vortex mixer then centrifuged at 14,500 rpm for 5 min. The supernatant was collected in a 4-mL clear glass vial, while the pellet (containing the polymeric thickener) was retained for further analysis. This thickener-free supernatant was then diluted 1:10 in THF and separated via gel permeation chromatography (GPC) with THF mobile phase. GPC separation results in fractionation of a sample by molecular mass, with higher molecular-weight components eluting before smaller components. Fractionation was performed using a Waters Corp. GPC system consisting of a 616 pump, 717 plus autosampler, and a 486 tunable UV detector. Polymer-free deicer samples (2 mL) were separated on tandem Envirogel (Waters Corp.) GPC columns (19 × 150 mm and 19 × 300 mm) at a flow rate of 5 mL/min. The GPC system was calibrated for retention times using a standardized mixture of corn oil, bis(2-ethylhexyl)phthalate, methoxychlor, perylene, and sulfur. The total run time was 26 min, with three fractions collected over the course of the separation. The first fraction was collected between 7.8 min and 13.3 min; the second fraction was collected from 13.3 min to 15.3 min; and the third fraction was collected from 15.3 min to 26.0 min. The fractions were collected in 40-mL amber vials. For each deicer, six fractionations were performed (corresponding to 1,200 μL of total deicer injected), and the collected fractions were pooled. The THF was evaporated from each combined fraction using a gentle stream of nitrogen gas.

Figure 3-2. Fractionation scheme for separating Type IV deicer products prior to toxicity assays and analytical characterization.



Each of the three fractions thus prepared was diluted to 1,100 µL with nanopure water prior to subsequent fractionation by reversed phase HPLC. Separations were performed on a semipreparative scale (250 × 10 mm, 5-µm particles) Aquasil C_{18} column (Thermo Scientific) using a Waters Corp. HPLC system (717 autosampler, 626 series pump, and 996 photodiode array detector). A solvent gradient was applied for separation, using nanopure water (solvent A) and methanol (solvent B). The program included a linear gradient from 0 to 100 percent B over 20 min with a subsequent 5 min hold at 100 percent B at a constant flow rate of 4 mL/min. Five subfractions were collected for each of the three GPC fractions. The fractions were collected from 4 min to 30 min into round-bottom flasks at 5-min increments. Two replicate injections of 500 µL each were performed for each GPC fraction (1,000 µL injected of 1,100 µL total). This HPLC separation procedure was performed for all three GPC fractions to yield 15 total fractions. These fractions were protected from light and concentrated to less than 500 µL by rotary evaporator. The fractions were then diluted to 1,200 µL in 50 percent methanol; 1,000 µL of each fraction was used for toxicity testing, and the remaining 200-µL amounts were reserved for chemical analysis.

This fractionation scheme was used to separate all four Type IV deicer products into 15 GPC/HPLC fractions plus one additional fraction of polymeric thickener (isolated by precipitation and resuspended in a minimal volume of nanopure water). An additional set of 15 samples was prepared as a GPC/HPLC system blank. The system blank samples were generated from six replicate 2-mL injections of THF onto the GPC system and carried through the subsequent steps of the HPLC fractionation.

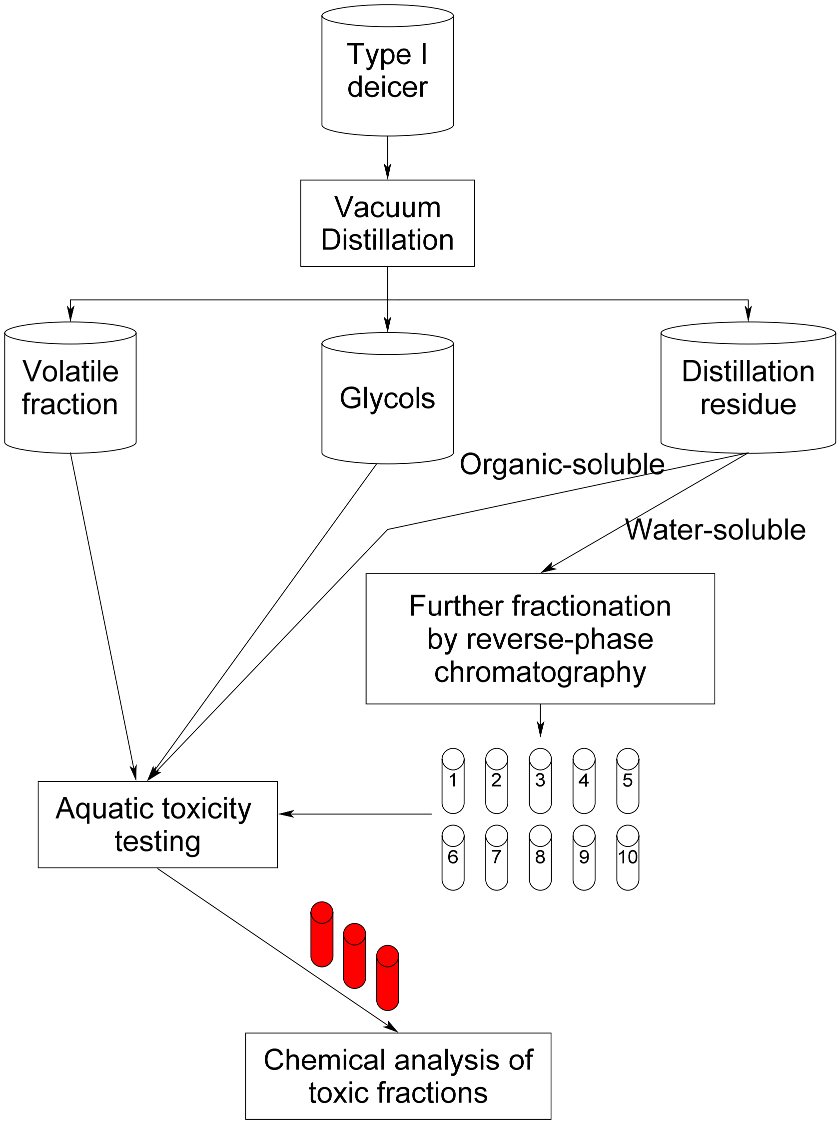
An additional, simplified fractionation was performed separately for the four Type IV deicer products selected for TIE. The fluids were subjected to centrifugal ultrafiltration (Millipore Centricon, 10,000 kDa MWCO) in order to separate the base deicer from its polymeric thickener without denaturing the thickener significantly. The resulting ultrafiltrate and retentate were then assayed for toxicity separately. The goal of this work was to identify the importance of the polymeric thickener in contributing to the toxicity of these deicer products.

Fractionation of Type I Deicer: Vacuum Distillation and HPLC Because of the considerably lower toxicity profiles of the Type I deicers investigated in the present work relative to the Type IV deicers (see toxicity results below), it was impractical to fractionate the Type I samples using the above GPC/HPLC methods. Such an endeavor would have required hundreds of individual injections and was cost- and labor-prohibitive. As an alternative, we employed a vacuum distillation protocol (Figure 3-3) as a primary fractionation method for the Type I deicers, with the goal of isolating the more volatile (and quantitatively dominant) water and glycol components from the minor components (e.g., additives). To this end, approximately 40.0 g of each Type I deicer fluid was weighed into a round-bottom flask containing crushed glass chips and a stir bar. The fluid was distilled with constant stirring under vacuum (Welch belt-drive rotary pump) with gentle and gradual heating using a bath of mineral oil. Distillates were collected from a chilled (4°C) condenser into two collection flasks.

The first collection flask was submerged in an ice bath, whereas the second collection flask was cooled by dry ice. The first distillation fraction was collected from room temperature (25°C) to an oil bath of ~65°C and vapor temperature ~35°C—this fraction was termed "volatiles" and was isolated by combining materials from both the ice-cooled and dry-ice-cooled collection flasks.

Distillate fraction 2 contained primarily glycols and was distilled at an oil bath temperature of ~90°C and a vapor temperature of ~65°C for those deicers containing PG and an oil bath temperature of ~100°C and a vapor temperature of ~75°C for those fluids containing EG.

Figure 3-3. Fractionation scheme for separating Type I deicer products prior to toxicity assays and analytical characterization.



The third fraction was isolated as the distillation residue remaining in the flask after removal of the first two fractions. This fraction was quantitatively transferred to a glass vial for further analysis by dissolution in a known volume of water and/or organic solvents (acetone or DMSO).

The HPLC fractionation was performed on the same instrumentation as described in the above for Type IV deicers separation scheme using the same column, mobile phase and gradient. Aliquots of the water-soluble distillation residue were diluted (10×) in nanopure water, and three replicate 500-µL injections were performed. Ten fractions were collected in round bottom flasks between 2 and 30 min, a separate fraction every 2.8 min. The samples were protected from light and concentrated by rotary evaporator to less than 500 µL. Samples were diluted to 1,200 µL in 50 percent methanol; 1,000 µL of each fraction was used for toxicity testing, and the remaining 200 µL of each fraction was reserved for chemical analysis.

Toxicity Assays of Deicer Fractions The toxicity of fractions of deicer formulations prepared as described above was characterized using the fathead minnow, *C. dubia,* and Microtox. To accommodate the large number of fractions, fathead minnow and *C. dubia* were combined in the same test vessel. Each fraction was tested with two replicates of five *C. dubia* and two fathead minnows per replicate. The tests were conducted in an environmental chamber with a 16-hour/8-hour light/dark cycle at 20°C. Test solutions were not renewed and water quality parameters were not monitored. Fraction assays were terminated and survival was recorded at 48 hours for both species. Microtox assays for the fractions were identical to the product testing procedures described above, with the exception of the addition of sodium chloride to a concentration of 2 percent, as required by the bacterium. Fraction toxicity was reported as toxic/nontoxic (based on a dose of ~400 percent of measured deicer product LC_{50}/EC_{50}) or, where dilutions were prepared, results were used to calculate an LC_{50} or EC_{50} in terms of the corresponding deicer product equivalent.

Analytical Methods ***Mass Spectrometric Analysis of Surfactants and Other Small Molecules*** A Waters API-US Quadropole time of flight (Q-TOF) mass spectrometer (Milford, Mass.) was used to determine masses of components of deicer and deicer fractions by electrospray mass spectrometry. Toxic deicer fractions prepared using both fractionation schemes (i.e., GPC-HPLC fractionation and distillation—HPLC fractionation) were diluted 1:50 in 50 percent methanol/0.1 percent formic acid for analysis. The samples thus prepared were infused at less than 1 µL/min using a syringe pump into a nano-electrospray ion source fitted with a concurrent nanospray emitter for constant production of sodium trifluoroacetate cluster ions (used as internal mass calibrants for accurate mass measurement of deicer fraction components). Positive ion electrospray mass spectra were acquired at 10,000 resolution (full width at half maximum) for each sample over a period of approximately 1 min with subsequent mass measurement and single-point lock-mass correction. Putative molecular formulas were assigned for candidate toxicants by applying a criterion of mass measurement accuracy better than 5 ppm.

A Bruker Ultraflex II Matrix-assisted laser desorption/ionization TOF/TOF (MALDI-TOF/TOF) (Billerica, Mass.) mass spectrometer was also used to determine the masses of compounds present in both deicers and deicer fractions. Toxic fractions of deicers prepared by both fractionation schemes were diluted as described above. Samples were prepared for MALDI analysis using the diluted fractions and neat deicer fluids by spotting the MALDI plate with 0.5 µL of a saturated α-cyano-4-cinnaminic acid (HCCA) solution and 0.5 µL of the diluted deicer or fraction sample. Mass spectra were acquired in reflectron mode by summing sequential shots from a 337-nm Nd:YAG laser.

Analysis of Polymeric Thickeners A straightforward gravimetric analysis method was used to analyze the amount of polymeric thickeners in the Type IV deicer products. Because the thickeners were found to be polyanionic materials, it was possible to precipitate them quantitatively by adding $CaCl_2$ to the neat Type IV deicer products. The precipitated thickeners were then washed extensively with ultrapure water and acetone before being dried under vacuum and weighed accurately (to 0.01 mg).

The polymeric thickener components of the Type IV deicers were characterized using Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy to identify the chemical class of these thickeners. The polymers were isolated from the fluids using several methods and were then compared spectroscopically to commercially available thickener candidates selected from Table 2-5. Candidates investigated included hydroxyethyl cellulose, carboxymethyl dextran, dextran, polyacrylic acid, gum arabic, xanthan gum, and welan gum.

Thickener isolates were analyzed using a Thermo Nicolet Nexus 670 FT-IR spectrometer with attenuated total reflectance (ATR) accessories to obtain characteristic FTIR spectra. Polymers were isolated from the Type IV deicers by both ultrafiltration (10,000-kDa membrane) and by precipitation using $CaCl_2$. The polymers thus obtained were washed and the residual solvents were evaporated to dryness using a centrifugal vacuum concentrator. The thickener isolates were then pressed against the sample aperture and analyzed by FT-ATR-IR in absorbance mode. Authentic standards of polymeric thickeners were analyzed in the same way.

Polymeric thickeners were also analyzed using a Varian Mercury/VX 400 NMR in order to obtain proton NMR spectra. Polymers were isolated from the Type IV deicers as described above. The thickener isolates and authentic standards (listed above) were diluted with d_2O and heated before and during analysis to ~80°C to enhance fluidity. Proton spectra were obtained using a 45° excitation pulse, 1.5 s relaxation delay, and FID acquisition time of 2.183 s.

^{13}C-NMR spectra of thickener isolates and authentic standards were obtained using a Varian Inova 500 NMR with a solids probe. Polymers were isolated from Type IV deicers as described above. The pellet of dried polymer was then ground to a fine powder. Powdered samples were introduced to the NMR in 30-µL sample cups and spectra were acquired through the solid state technique of cross polarization with tangentially ramped ^{13}C spin lock using a Coty XC MAS probe. Protons were decoupled with two pulse phase modulation MAS spinning at 10 kHz; cross-polarization contact time was 1.5 ms, and relaxation delay was 1.5 s. Polymer standard materials were analyzed directly in powdered form with the exception of the polyacrylic acid polymers which were first mixed in water and then precipitated from solution before analysis.

Quantitative Analysis of APE Surfactants Analysis of pure Type I deicers and polymer-free Type IV deicers was performed to determine the concentrations of APE surfactants in the neat fluids. APE surfactants were measured using HPLC-ESI-MS essentially as described previously (Ferguson et al., 2001; Loyo-Rosales et al., 2003). Samples of Type I deicers were prepared by dilution of the fluid by a factor of 10–50 in starting mobile phase. Type IV deicers were precipitated by addition of 100 µL of 10 M $CaCl_2$ to remove polymeric thickener prior to dilution (factor of 10–50) and HPLC-MS analysis. An Agilent 1100 chromatography system was interfaced to a Micromass Quattro-LC tandem MS instrument through an ESI source. The analytical column used for separations of APEs was a Shodex MSpak GF-310 4D, 4.6 × 150 mm column. The column was maintained at 60°C, and the solvent flow rate was 0.2 mL/min. Solvent A consisted of 500 µM of ammonium acetate in 90 percent nanopure water with 10 percent methanol. Solvent B consisted of 500 µM of ammonium acetate in methanol. The mobile phase gradient began at 50 percent B and over 22.7 min was ramped to 100 percent B, where it was held for 10 min. The gradient was then ramped to 0 percent B from 32.7 min to 38 min and held at 0 percent B for 2 min. Initial conditions were returned (50 percent B) by 45 min and equilibrated for 10 min for a total run time of 55 min. Data were acquired in full scan mode alternating between positive and negative ionization modes. Quantitation of APE surfactants was performed using the ammonium ion adducts of APE ethoxymers, whereas quantitation of alkylphenols was performed in negative ion mode by observing deprotonated alkylphenolate ions. Calibration curves were prepared in mobile phase A for analytes and internal standards and were linear over the range of calibration. The concentration of individual ethoxylate analytes in the standards varied due to the polydispersed nature of the ethoxylated standard materials.

In general, the concentrations of NPEs ranged from 20 ng/mL (NP1EO) and 0.07 ng/mL (NP17EO) in the lowest standard to 3,000 ng/mL (NP1EO) and 11 ng/mL (NP17EO) in the highest concentration standard. OPE concentrations ranged from 1.3 ng/mL (OP1EO) and 0.017 ng/mL (OP17EO) in the lowest concentration standard to 2,000 ng/mL (OP1EO) and 13 ng/mL (OP17EO) in the highest concentration standard. Quantitation of NPEOs and OPEOs was based on the relative responses of the analytes to their corresponding internal standards, which were synthetic $^{13}C_6$-labeled NP and NPEOs, added to both calibration standards and analytical samples prior to analysis. All analytical determinations were conducted in triplicate. Because the analyses were conducted in full-scan MS mode, it was also possible to observe polyethoxylated aliphatic surfactants in the deicer formulations during the course of the HPLC-MS runs. These data were used to confirm surfactant identifications obtained by electrospray Q-TOF mass spectrometry (described above), and it was possible to estimate relative abundances and average levels of ethoxylation of the various surfactant classes by measuring mass spectral response (i.e., chromatographic peak areas) in the deicer samples.

Quantitative Analysis of Corrosion Inhibitors Fourteen deicer products (including pavement deicers) were analyzed for the presence of benzotriazole corrosion inhibitors using HPLC MS/MS. The four corrosion inhibitors analyzed were 1H-benzotriazole (1H-BT), 4-methyl-1H-benzotriazole (4-MeBT), 5-methyl-1H-benzotriazole (5-MeBT), and 5,6-dimethyl-benzotriazole (5,6-diMeBT). Samples were prepared by diluting the deicers with an acetonitrile and ammonium acetate buffer, and caffeine was added as the internal standard. The separation was performed on an Agilent 1100 HPLC using a Zorbax Eclipse XDB-C18 column and a water and acetonitrile mobile phase with 0.1 percent formic acid in both. The positive electrospray analysis was performed on an Applied Biosystems API 2000 MS/MS instrument. Calibration curves were prepared containing all the internal standard and three analytes; concentrations ranged from 0.03 µg/L to 2900 µg/L. The standards for 1H-BT, 5-MeBT and 5,6-diMeBT are commercially available and purchased from Sigma-Aldrich; however, a standard for 4-MeBT is not commercially available. The quantitation of 4-MeBT was performed using the calibration curve generated from 5-MeBT standards.

Results

Baseline Acute Toxicity Testing Five Type I products were assayed to generate LC_{50}s for regulatory species (Figure 3-4). Two additional Type I products were assayed using range-finding tests to get a general idea of toxicity (data not shown). LC_{50}s fell into two categories. One group of five Type I products resulted in LC_{50}s averaging about 10,000 mg/L, whereas two products showed less toxicity, with LC_{50}s near 30,000 mg/L. Type IV deicer products consistently demonstrated much greater toxicity than the Type I products, with LC_{50}s near 2,500 mg/L and lower (Figure 3-5). For both Type I and Type IV deicer products, toxicity results with marine species was similar to those using freshwater test species (Figures 3-4 and 3-5). Three types of pavement deicer/anti-icer were tested for acute aquatic toxicity and results indicate differences based on the FPD listed as the main ingredient. The three FPDs used in pavement deicers were assayed as pure chemicals for comparison (Figure 3-6). Keeping in mind that the potassium acetate PDM is 50% FPD, results are similar between the FPDs and formulated products except for the Microtox results for sodium formate. For this formulation, the formulated product had a substantially lower EC_{50} than the FPD suggesting influence of an additive component. From least toxic to most toxic, the pavement deicer FPDs ranked in the following order as measured by weight per volume: sodium acetate, sodium formate, potassium acetate.

Results of Microtox testing indicated that Type I products were not especially toxic in this test with EC_{50}s >20,000 mg/L (Figure 3-4). The Microtox test results for Type IV products indicated more sensitivity with results ranging from 338 mg/L to 13,800 mg/L. For pavement deicers, EC_{50}s from Microtox testing varied between 816 mg/L to 62,400 mg/L.

Test results for pavement deicers indicate that toxicity was due primarily to the FPDs rather than additives, except in the case of Microtox results for product N. The source of this observed toxicity is unknown, but could be associated with corrosion inhibitors or anticaking agents contained in solid forms of PDM. Based on overall PDM test results, no further testing or fractionation was conducted to evaluate toxicity of pavement deicers.

Figure 3-4. Acute test lethal concentrations (LC$_{50}$s) for Type I deicer products for Microtox and four regulatory species tested. Error bars indicate 95% confidence interval.

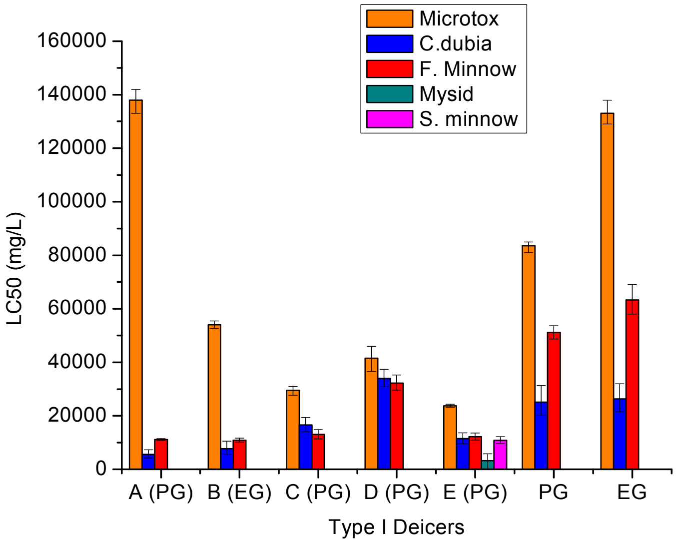


Figure 3-5. Acute test lethal concentrations (LC$_{50}$s) for Type IV deicer products for Microtox and four regulatory species tested. Error bars indicate 95% confidence interval.

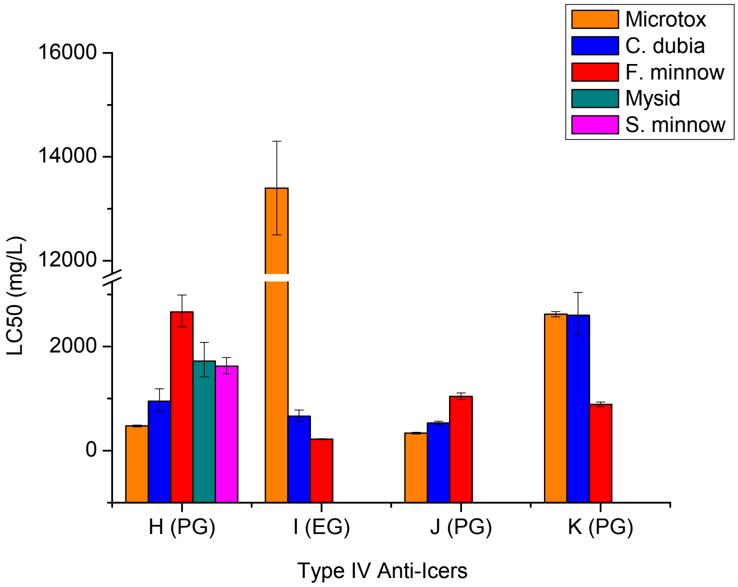
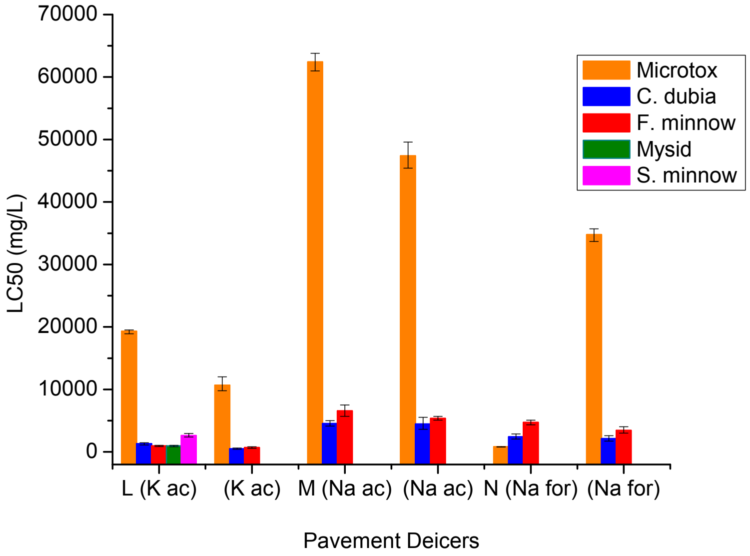


Figure 3-6. Acute toxicity test lethal concentrations (LC$_{50}$s) for pavement deicer products for Microtox and four regulatory species tested. Error bars indicate 95% confidence interval.



Baseline Chronic Toxicity Testing Five Type I products were assayed to generate IC$_{25}$s for regulatory species (Figure 3-7). Four of the five products had IC$_{25}$s less than 4,000 mg/L for at least two of the three organisms. These same four formulations had IC$_{25}$s of 309 mg/L or less for at least one organism. IC$_{25}$s for the fifth Type I product were 5,680 mg/L or greater for the tested organisms. Type IV deicer products consistently demonstrated much greater toxicity than the Type I products, with IC$_{25}$s between 80 mg/L and 1,350 mg/L (Figure 3-8). Three types of pavement deicer/anti-icer and pure potassium acetate and sodium formate were tested for chronic aquatic toxicity. Similar to the acute toxicity results, the chronic toxicity results indicate differences based on the FPD listed as the main ingredient for potassium acetate and sodium formate (Figure 3-9). The FPD sodium acetate was not tested for chronic toxicity. *C. dubia* and algae were more sensitive to all three PDM formulations than were fathead minnows.

Figure 3-7. Chronic test lethal concentrations (IC_{25}s) for Type I deicer products for three regulatory species tested. Error bars indicate 95% confidence interval.

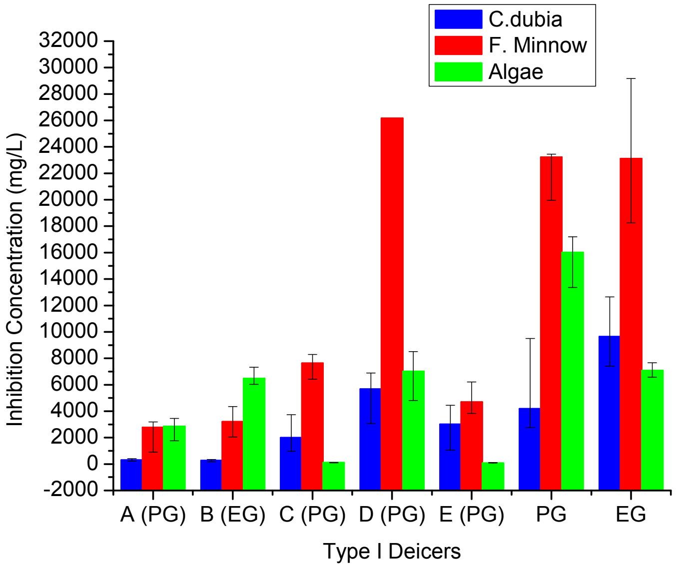


Figure 3-8. Chronic test lethal concentrations (IC$_{25}$s) for Type IV deicer products for three regulatory species tested. Error bars indicate 95% confidence interval.

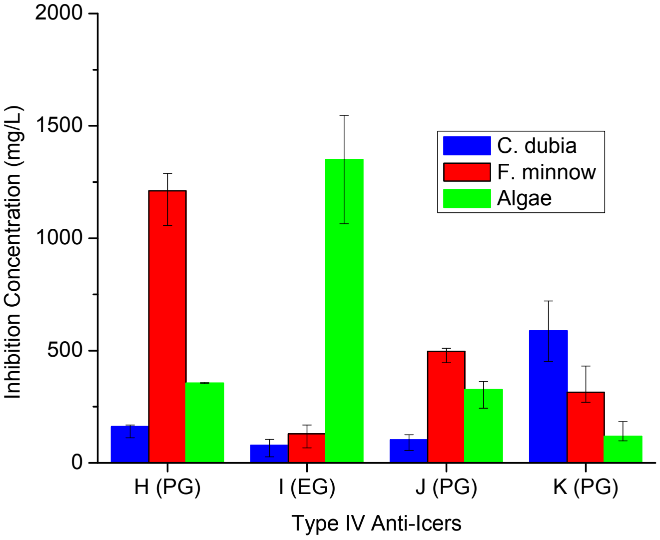
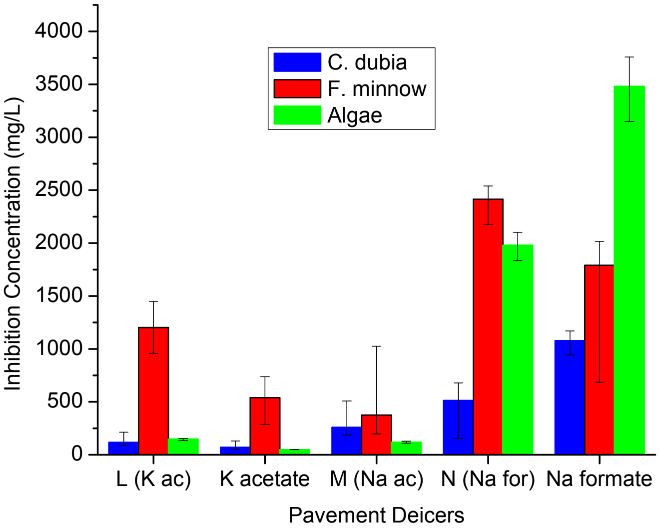


Figure 3-9. Chronic test lethal concentrations (IC$_{25}$s) for pavement deicer products for three regulatory species tested. Error bars indicate 95% confidence interval.



TIE Results The TIE process described in the methods above resulted in numerous fractions for each deicer product, all of which were assessed for toxicity using a three-tier bioassay approach. The general strategy applied in interpreting the TIE results was to focus analytical efforts on fractions showing significant toxicity. The results of these analyses were used to guide further quantitative analysis of candidate toxicants in the neat deicer formulations. The most important results obtained from the TIE work are summarized in the following subsections.

Type IV Deicer Products Initial TIE work focused on the Type IV deicer products because these were found to be the most toxic formulations (as described above). Table 3-2 summarizes the results of toxicity assays conducted on Type IV fluids fractionated using the GPC/HPLC approach. This approach generated fifteen individual fractions plus an additional fraction containing the precipitated polymeric thickener. Significant toxicity was observed in control "blank" fractionations (essentially consisting of only THF solvent subjected to the same GPC/HPLC and sample handling protocols used for the deicer products) for fractions 1, 6, 11, and 12. These fractions represent the most polar (least hydrophobic) compounds eluted from the reverse-phase HPLC separation for each of the three GPC fractionations. It is hypothesized that this toxicity was due to impurities (e.g., organic peroxides) in the THF solvent used in the GPC separation or to extractables leached from the seals in the HPLC system. Regardless, this blank-associated toxicity precluded identification of any toxic components present in fractions 1, 6, 11, or 12 of the deicer products. Nevertheless, significant toxicity was observed in several additional fractions for each of the Type IV deicer products tested by TIE. Specifically, fraction 5 showed consistent toxicity in all four of the products for all species tested (except for fathead minnows in product H). Several fractions showed isolated, non blank-associated toxicity for individual products. Examples include the polymeric thickener in product K (Microtox); fraction 10 in products K and H; fraction 8 in product K (Microtox); fraction 2 in products K, I, and H; and fraction 7 in products K and I. Slight toxicity was observed in fractions 14 and 15 from product K.

TABLE 3-2 Summary of Toxicity Results from GPC/HPLC Fractionation of Type IV Deicer Products

	Blank 1			**Blank 2**			**Product K**			**Product J**			**Product I**			**Product H**		
Fraction*	**M**	**C**	**F**	**M**	**C**	**F**	**M**	**C**	**F**	**M**	**C**	**F**	**M**	**C**	**F**	**M**	**C**	**F**
MeOH control	80	100	100	84	100	100	78	100	100	78	100	100	76	100	100	77	90	100
1	2	0	0	24	0	100	0	0	0	8	0	0	0	0	75	6	0	0
2	73	100	100	64	100	100	37	0	100	76	100	75	20	100	100	41	0	100
3	72	100	75	82	100	100	68	100	100	79	100	100	91	100	100	85	100	100
4	73	100	100	83	100	100	80	100	100	80	100	100	74	100	100	74	90	100
5	76	100	100	82	100	100	0	0	0	37	0	0	9	0	0	38	20	100
6	80	100	100	63	0	100	2	0	0	22	0	100	0	0	100	25	0	100
7	72	100	100	86	100	100	29	0	100	63	100	100	19	100	100	78	100	100
8	69	100	100	78	90	100	35	100	75	75	100	100	99	100	100	68	100	100
9	82	100	100	88	100	100	84	100	100	77	100	100	—	—	—	84	100	100
10	79	100	100	89	40	100	61	0	0	82	100	100	86	100	100	29	20	75
11	0	0	0	0	0	0	0	0	0	1	0	0	0	0	100	4	0	0
12	25	0	100	33	0	100	41	0	100	59	70	100	15	100	100	77	100	100
13	78	100	100	35	80	100	80	100	100	79	100	100	137	100	100	77	100	100
14	75	100	100	81	100	100	56	100	100	75	100	100	108	100	100	79	90	75
15	64	100	100	84	100	100	46	100	75	78	100	100	113	100	100	79	100	100
Thickener	—	—	—	—	—	—	30	100	100	77	100	100	82	100	100	66	100	100

Values correspond to percent survival. Green cells are nontoxic fractions, red cells are toxic fractions, and orange cells are fractions exhibiting slight toxicity. Fraction toxicity was assayed at 400 percent equivalent of measured LC_{50} values of the respective deicer product. M, Microtox; C, *Ceriodaphnia dubia*; F, fathead minnow. Fraction numbers correspond to those in Figure 3-2.

Analyses of the toxic fractions identified in Table 3-2 were conducted by MS methods to identify major chemical components that may have contributed to the observed toxic effects. To this end, high-resolution electrospray quadrupole/TOF MS and MALDI-TOF MS were used to enable the most comprehensive qualitative analysis possible. These techniques are appropriate for detecting most semivolatile or nonvolatile chemical species expected to be present in deicer formulations. Results are summarized in Table 3-3. As mentioned above, the most consistent toxicity observed for the four Type IV deicer products tested was associated with TIE fraction 5. This fraction was observed to contain primarily ethoxylated surfactants in all four products. The suite of ethoxylated surfactants identified in fraction 5 differed considerably among the four products tested. Product K's fraction 5 contained OPE with detectable ethoxy-chain lengths ranging from 2-9, NPE with ethoxy-chain lengths ranging from 4 to 24, and an aliphatic alcohol ethoxylate ($C_{16}EO$) with a 16-carbon hydrophobe and ethoxy-chain lengths ranging from 3 to 6. Product J's fraction 5 contained nonionic ethoxylated surfactants having only aliphatic hydrophobes (with 10-, 12-, and 14-carbon alcohol bases) and ethoxy-chain lengths ranging from 2 to 19 (slightly variable among the three hydrophobe bases). Product I contained NPE with ethoxy-chain lengths ranging from 2 to 18 and two aliphatic alcohol ethoxylate surfactants with 13-carbon ($C_{13}EO$) and 16-carbon ($C_{16}EO$) hydrophobes and ethoxy-chain lengths ranging from 15 to 19 and from 3 to 13, respectively. Fraction 5 isolated from product H contained only two aliphatic alcohol ethoxylate series, with 12-carbon and 14-carbon hydrophobes ($C_{12}EO$ and $C_{14}EO$) and ethoxy-chain lengths ranging from 5 to 19 and from 4 to 18, respectively. For products K and H, analyses of fraction 10 indicated that this fraction also contained nonionic polyethoxylated surfactants. This result is consistent with the limited chromatographic resolution of the GPC separation used in fractionation; i.e., incomplete separation of the polyethoxylated surfactant series by GPC would lead to the presence of these compounds in multiple corresponding fractions of the second (reverse-phase HPLC) stage of the TIE fractionation scheme. Toxic fraction 8 in product K was found to contain methyl-1H-benzotriazole.

For selected chemical classes identified in toxic fractions, accurate-mass measurement was conducted by electrospray Q-TOF MS in order to confirm the elemental composition (and thereby verify the chemical identity) of putative components. For all accurate mass measurements, analytical values matched theoretical mass values to an accuracy better than 5 ppm, thereby verifying the postulated elemental formulae for candidate toxicants (Table 3-3).

Several toxic fractions isolated from the TIE scheme for Type IV deicer products did not yield definitive chemical component identities. Specifically, fractions 2 and 7 showed toxicity in several TIE fractionations from deicer products, but no specific molecular species were identified in these fractions that were not also associated with the corresponding fractions from blank TIE fractionations. The toxicity observed in these two fractions may have been associated with carryover of artifactual toxicants from fractions 1 and 6 (these exhibited toxicity in blank fractionations), although there are not enough data to verify this postulation.

TABLE 3-3 Summary of Major Chemical Components Identified in Toxic GPC/HPLC Fractions Isolated from Type IV Deicer Products

Deicer	Fraction No.[a]	Compounds Identified in Fraction[b]
Product K	5	OPE 2-9,[c] NPE 4-24,[c] C_{16}EO 3-6[c]
	8	methyl-1H-benzotriazole[c]
	10	OPE 2-5
Product J	5	C_{10}EO 5-16,[c] C_{12}EO 2-19,[c] C_{14}EO 2-17[c]
Product I	5	NPE 2-18,[c] C_{13}EO 15-19,[c] C_{16}EO 3-13[c]
Product H	5	C_{12}EO 5-19, C_{14}EO 4-18
	10	C_{12}EO 2-6

[a] Fraction numbers correspond to those in Figure 3-2.
[b] See text for chemical nomenclature.
[c] Compound identities confirmed by accurate mass measurement (better than 5-ppm mass accuracy) using electrospray Q-TOF MS.

In the course of conducting TIE evaluations of Type IV deicer products, it was observed that the summed toxicities of all fractions isolated through the separation scheme did not typically total the original toxicity of the unfractionated product. This inconsistency could have been due to either non-additive toxicity of chemical components of the fluids, to losses of specific toxicants through the TIE fractionation scheme, or to toxicants distributed through more than one fraction, thereby diluting the toxicity signal. Several laboratory tests suggested the polymeric thickener as a potential contributor to Type IV deicer product toxicity. Although thickener toxicity was only observed in product K for Microtox assays in the GPC/HPLC TIE scheme (Table 3-2), it was noted that the preparation of the thickener for toxicity testing involved isolating it from the product by solvent precipitation (thus denaturing the polymer). This treatment may have introduced considerable alterations to the toxicity profile of the polymeric thickener.

The contribution of the polymeric thickener to Type IV deicer product toxicity was assayed by using a nondenaturing ultrafiltration step to selectively isolate the (high-molecular-weight) polymeric thickener from the (lower molecular weight) remaining components of the fluids. The isolates thus obtained were then tested for toxicity separately and after recombination and were then compared to the toxicity of the products prior to ultrafiltration. Results (Table 3-4) indicated that high-molecular-weight components isolated with the polymeric thickener through ultrafiltration contributed to the toxicity of all four Type IV deicer products tested. For product K, the high-molecular-weight isolate accounted for approximately half of the toxicity of the neat deicer for *C. dubia* and fathead minnows, but no detectable toxicity was observed for this fraction in the Microtox test. This result is in direct contradiction to results from the GPC/HPLC TIE fractionation (Table 3-2); and may reflect the considerable differences between toxicity profiles of denatured and non-denatured polymeric thickeners isolated from the deicer product by the two methods. The high-molecular-weight fraction isolated by ultrafiltration accounted for virtually all of the detectable toxicity of product J when compared to the low-molecular-weight ultrafiltrate (nontoxic at the highest dose tested). The GPC/HPLC TIE profile of this deicer product had previously indicated only toxicity associated with fractions containing nonionic surfactants

(Tables 3-2 and 3-3). The high-molecular-weight ultrafiltration isolate from Type IV deicer product I also seemed to have contributed significantly to the toxicity of this deicer (Table 3-4). In this case, the low-molecular-weight ultrafiltrate was also toxic to all three bioassay species tested, albeit at higher test concentrations. Finally, the high-molecular-weight isolate from product H was toxic to Microtox and *C. dubia* but relatively less toxic to fathead minnows, compared to the unfiltered product. The low-molecular-weight ultrafiltrate of product H accounted for less of the unfiltered product's toxicity to Microtox and *C. dubia* than did the high-molecular-weight isolate and was practically nontoxic to fathead minnows at the highest concentration tested. Overall, for most of the Type IV deicer products tested by ultrafiltration, the recombined low- and high-molecular-weight fractions gave toxicity results that were similar to those obtained for the unfiltered deicer product, indicating that the ultrafiltration process did not introduce significant artifacts into the subsequent toxicity testing. It should be noted, however, that the ultrafiltration process may not have resulted in complete separation of high-molecular-weight components from low-molecular-weight compounds (e.g., polymeric thickener from surfactants), as it is possible that these components may interact strongly in solution, leading to imperfect separation during the filtration. Semiquantitative chemical analysis of both low- and high-molecular weight fractions indicated the presence of surfactants in both isolates in all four Type IV deicer products tested; therefore, it is possible that these components (and perhaps others) could have influenced toxicity of both ultrafiltration fractions.

TABLE 3-4 Contribution of High Molecular Weight (>10,000 MWCO) Components to Toxicity of Type IV Deicer Products

	Product K			**Product J**			**Product I**			**Product H**		
	M	**C**	**F**	**M**	**C**	**F**	**M**	**C**	**F**	**M**	**C**	**F**
Deicer product	3,792	3,712	1,857	300	789	1,751	1314	896	296	478	1,531	4,331
Low molecular weight (1)	4,324	5,627	3,122	>4,164	>4,164	>4,164	2,986	4,729	1,988	4,888	6,961	>10,664
High molecular weight (2)	>10,500	5,627	3,712	474	846	2,944	279	1,182	351	1,263	2,321	10,664
Combined (1+2)	3,354	3,712	1,857	371	789	2,082	932	780	296	1,000	2,321	6,341

Values represent EC_{50} (Microtox) or LC_{50} (*Ceriodaphnia dubia*, fathead minnow) in mg/L. M, Microtox; C, *Ceriodaphnia dubia*; F, fathead minnow.

Type I Deicer Products Type I deicer products were fractionated using a two-step distillation/HPLC method (Figure 3-3), and the fractions thus obtained were assayed for toxicity using a three-tier bioassay testing scheme. Specifically, the deicer products were separated into highly volatile (mostly water) fractions, glycol-containing fractions, and nonvolatile fractions by distillation. The nonvolatile fraction was then separated into a water-soluble and organic solvent-soluble fraction. The water-soluble fraction was subsequently fractionated by HPLC. Results (Table 3-5) indicated that the fractionation method did not consistently result in recovery of all toxicity. The highly volatile fraction isolated from distillation of Type I deicer products did not result in toxicity to any species for any of the tested products. This result is consistent with the hypothesis that this fraction was composed primarily of water. Separation of glycol from the products during distillation was confirmed with toxicity results matching the expected LC_{50} of glycol (Figure 3-4) in three of the products (product C glycol fraction had a higher LC_{50} because it is a ready-to-use, or diluted, product). Unlike in the case of the Type IV deicer product TIE approach discussed above, no significant blank toxicity was observed in tests using the HPLC conditions applied to fractionation of Type I deicer products.

Overall, very little toxicity was observed for either the organic-soluble or HPLC-separated fractions for any of the products tested (Table 3-5). In general, not enough toxicity was observed in the TIE approach for Type I deicer products to account for the LC_{50} of the original products. However, analytical results for selected toxic fractions did reveal specific components of the deicer products that may contribute to aquatic toxicity (Table 3-6). Specifically, product A and product C both had toxicity associated with the organic-soluble fraction from the distillation. These fractions were found to contain ethoxylated aliphatic alcohol surfactants. Product A's organic-soluble fraction contained 10-carbon and 12-carbon alcohol hydrophobes with ethoxy-chain lengths ranging from 5 to 16 and 5 to 12, respectively. The organic-soluble fraction isolated from product C contained polyethoxylated alcohol surfactants having aliphatic hydrophobes with 13-, 14-, 15-, and 16-carbons and ethoxy-chain lengths ranging from 8 to 23. HPLC fractions 9 and 10 from deicer product E were toxic or slightly toxic to all three bioassay species, and these fractions were found to contain polyethoxylated alcohol surfactants having aliphatic hydrophobes with 12-, 13-, and 14-carbons and ethoxy-chain lengths ranging from 6 to 19. HPLC fractions 1–3 of deicer product B were toxic to *C. dubia*, but no specific compounds could be isolated analytically from these fractions to explain the toxicity. It is possible that these results were spurious or artifactual. HPLC fraction 10 from product B was not significantly toxic but it did induce a slight response in all three bioassays (Table 3-5). This fraction also contained 10-carbon and 12-carbon alcohol hydrophobes with ethoxy-chain lengths ranging from 5 to 16 and from 5 to 12, respectively (Table 3-6; similar to the organic-soluble fraction of product A). The surfactants have been identified as components of concern in most current formulations. Overall, it was not possible to account for the full toxicity of Type I deicer products through toxicity testing of TIE fractions. Detailed mass balance studies failed to discover artifacts introduced during the distillation step that may have led to losses of toxic components. It is possible that components of Type I deicers exert full toxicity only when in formulated mixture (i.e., synergistic toxicity), although verification of such a phenomenon would require additional work beyond the scope of this project.

TABLE 3-5 Summary of Toxicity Results from Distillation/HPLC Fractionation of Type I Deicer Products

	Blank			**Product A**			**Product B**			**Product C**			**Product E**		
Fraction[a]	**M**	**C**	**F**	**M**	**C**	**F**	**M**	**C**	**F**	**M**	**C**	**F**	**M**	**C**	**F**
Volatiles[b]	n/a	n/a	n/a	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
Glycol[b]	n/a	n/a	n/a	42,000	44,000	47,000	50,000	36,000	23,000	>111,000	76,000	79,000	>64,000	45,000	64,000
Organic-soluble[b]	n/a	n/a	n/a	NT	NT	67,000	NT	NT	NT	NT	NT	79,000	NT	NT	NT
MeOH control	80	100	100	77	100	100	74	100	100	77	90	100	81	100	100
HPLC F1	66	100	100	88	100	100	86	0	100	79	100	75	81	90	100
F2	80	100	100	87	80	100	96	0	100	69	100	75	81	100	100
F3	67	100	100	76	100	100	82	0	100	42	70	100	73	100	100
F4	73	100	100	74	100	100	74	100	100	59	80	75	77	100	100
F5	76	100	100	68	100	75	70	100	100	74	100	100	78	100	100
F6	74	100	100	75	100	75	66	100	100	78	100	100	78	90	100
F7	71	100	100	77	100	100	67	100	100	80	100	100	72	100	100
F8	69	100	100	59	100	100	77	100	100	50	100	100	77	100	100
F9	76	100	100	71	100	100	66	90	75	70	80	100	47	60	25
F10	58	100	100	78	100	100	64	80	75	81	80	100	53	30	0
Fraction test concentrations[c]					160,320			133,440			133,440			153,600	

Values correspond to percent survival unless noted otherwise. Green cells represent non-toxic fractions, red cells indicate toxic fractions, and orange cells represent fractions exhibiting slight toxicity. Fraction toxicity test concentrations are given. Toxicity values for pure glycols are from Pillard et al. (1995). M, Microtox; C, *Ceriodaphnia dubia*; F, fathead minnow.

[a] Fraction numbers correspond to those in Figure 3-3

[b] Tabulated values correspond to measured LC_{50} (C&F) or EC_{50} (M) values

[c] Fraction concentrations expressed as deicer equivalent.

TABLE 3-6 Summary of Major Chemical Components Identified in Toxic Distillation/HPLC Fractions Isolated from Type I Deicer Products

Deicer	Fraction[a]	Compounds Identified in Fraction[b]
Product A	Organic soluble	C_{10}EO 5-16
		C_{12}EO 5-12
Product B	10	C_{10}EO 5-16
		C_{12}EO 5-16
Product C	Organic soluble	C_{13}EO 9-15
		C_{14}EO 9-20
		C_{15}EO 8-23
		C_{16}EO 8-22
Product E	9, 10	C_{12}EO 6-17
		C_{13}EO 6-19
		C_{14}EO 6-17

[a] Fraction numbers correspond to those in Figure 3-3.
[b] Chemical nomenclature: see text for explanation.

Targeted Analyses *Semiquantitative Analysis of Ethoxylated Surfactants in Deicer Products*

Based on the results of the TIE approach described above, it became clear that polyethoxylated nonionic surfactants were of concern with regard to toxicity contribution to the commercial Type I and Type IV deicer products tested. Therefore, HPLC-MS approaches were utilized to characterize the suite of polyethoxylated nonionic surfactants present in these products. Table 3-7 summarizes the results of these analyses. For each product, the suite of nonionic surfactant series' that are present were tabulated, along with the estimated average ethoxy-chain length (the EO number) for each, and the estimated relative abundance of the individual surfactant series' within a given product. The surfactant identity nomenclature is such that the aliphatic alcohol ethoxylates are denoted as C_XEO Y-Z, where X = the number of carbons in the alcohol hydrophobe and Y - Z = the range of ethoxy-chain length observed in the HPLC-MS analyses. APEs are denoted NPE or OPE for nonylphenol and octylphenol hydrophobes, respectively, with the same notation as alcohol ethoxylates with respect to ethoxy-chain length. The average EO number is a measure of the hydrophobe-lipophobe balance of the surfactant series, and has been estimated here for each surfactant using the integrated HPLC-MS peak areas. It should be noted that such estimation suffers from inaccuracies due to variability in the instrument response for each EO within a single surfactant series. However, the values tabulated here are most likely accurate to within a range of 1–3 EO numbers. In addition, the relative spectral abundance values are intended to indicate the most prevalent nonionic surfactant series within a given product, and are not corrected for differences in spectral response among classes. Such correction requires authentic standards for each surfactant series. Unfortunately, calibrated reference standards of the alcohol ethoxylate surfactants identified in the deicer products through TIE work were not available, and therefore quantitative measurements of these deicer components was not possible.

Several conclusions can be drawn from the data presented in Table 3-7. All of the products contained one or more classes of polyethoxylated nonionic surfactants, and among these series, most had average EO numbers less than 10. These are relatively low average-molecular-weight surfactants, similar to those used in many other commercial applications such as detergents and hard-surface cleaners. Type I deicer products tested did not contain alkylphenol polyethoxylate surfactants, whereas two of the Type IV deicer products tested contained almost exclusively these APE-based surfactants.

Type I deicer products A and B contained only a very simple mixture of ethoxylated surfactants, quantitatively dominated by C_{12} alcohol ethoxylates having ethoxy-chain lengths ranging < 20. Product C had a more complex surfactant suite, composed of a mixture of alcohol ethoxylate surfactants dominated by C_{14} and C_{15} hydrophobes and with significant quantities of C_{12}-, C_{13}-, and C_{16}-based polyethoxylates. The maximum extent of ethoxylation observed for this product was > 25 units. The polyethoxylated surfactants in product E were dominated by alcohol ethoxylates with C_{12-14} hydrophobes and smaller quantities of C_{10}EO surfactants. All of these had ethoxy-chains ranging up to < 20 units in length. Type IV deicer products H and J contained primarily C_{12} and C_{14} alcohol ethoxylates with ethoxy-chain lengths ranging up to < 20 units. The dominant surfactant in product I was nonylphenol polyethoxylate series with a maximum ethoxy-chain length < 20, whereas product K had mostly octylphenol polyethoxylates with relatively small range of ethoxy-chain lengths (up to < 10).

TABLE 3-7 Summary of Surfactants Identified in Type I and Type IV Deicer Products by Q-TOF, MALDI, and LC-MS Mass Spectrometry Techniques

Deicer	Surfactants Identified[a]	Estimated Average EO Number[b]	Relative Spectral Abundance[c]
Product A[d]	C_{10}EO 3-18	10.16	1
	C_{12}EO 1-17	6.82	100
Product B[d]	C_{9}EO 2-12	2.59	1
	C_{10}EO 3-16	10.09	1
	C_{12}EO 1-17	7.10	100
Product C[d]	C_{12}EO 1-17	6.11	25
	C_{13}EO 9-21	9.14	58
	C_{14}EO 9-26	9.94	98
	C_{15}EO 8-27	10.16	100
	C_{16}EO 8-25	10.74	72
Product E[d]	C_{10}EO 1-18	9.00	12
	C_{11}EO 1-19	8.92	5
	C_{12}EO 1-18	9.34	42
	C_{13}EO 1-19	8.94	100
	C_{14}EO 1-17	8.50	50
	C_{15}EO 1-17	9.24	4
	C_{16}EO 1-16	5.73	1

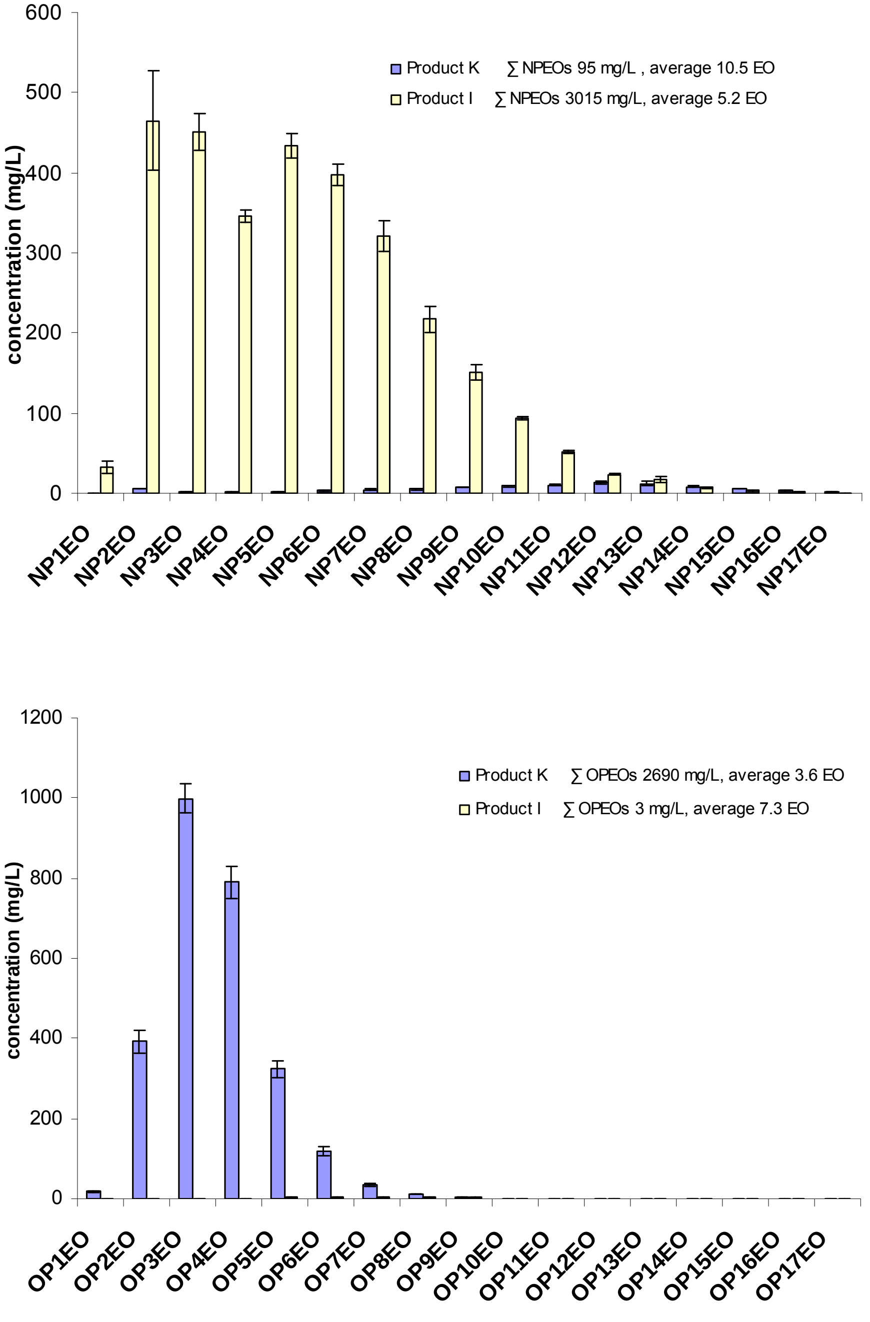
TABLE 3-7 Summary of Surfactants Identified in Type I and Type IV Deicer Products by Q-TOF, MALDI, and LC-MS Mass Spectrometry Techniques

Deicer	Surfactants Identified[a]	Estimated Average EO Number[b]	Relative Spectral Abundance[c]
Product H[e]	C_{10}EO 2-19	6.13	2
	C_{11}EO 2-18	8.13	1
	C_{12}EO 1-20	6.08	100
	C_{13}EO 1-17	6.08	3
	C_{14}EO 1-18	6.66	19
	C_{15}EO 1-17	9.53	5
	C_{16}EO 1-5	2.85	1
Product I[e]	OPE 5-13	7.33	1
	NPE 1-18*	5.24	100
	C_{13}EO 1-19*	7.69	0.3
	C_{16}EO 1-16*	7.16	2
Product J[e]	C_{10}EO 2-16*	7.07	2
	C_{11}EO 4-18	9.20	1
	C_{12}EO 1-19*	6.79	100
	C_{14}EO 2-17*	7.12	16
	C_{15}EO 1-17	9.49	3
	C_{16}EO 1-9	3.23	1
Product K[e]	OPE 2-9*	3.59	100
	NPE 4-24*	10.48	7
	C_{10}EO 3-18	9.86	1
	C_{12}EO 1-17	5.73	1
	C_{15}EO 1-17	6.61	3
	C_{16}EO 1-8*	4.58	0.1

[a] Chemical nomenclature: see text for explanation.
[b] Average EO number: calculated as the estimated average length of the polyethoxylate hydrophilic chain for a given surfactant series based on mass spectral intensities.
[c] Relative spectral abundance: based on integrated LC-MS peak areas. The highest abundance numbers correspond to the most prevalent surfactant series in a given product.
[d] Type I fluid
[e] Type I fluid
*Compound identities confirmed by accurate mass measurement (better than 5 ppm mass accuracy) using electrospray Q-TOF MS.

Quantitative Analysis of APEs in Type IV Deicer Products I and K Because of the known toxicity and significant concerns about environmental impacts of alkylphenol polyethoxylate surfactants (discussed in Section 2) as well as the finding that these components were present in toxic TIE fractions of selected deicer products (above), we conducted quantitative analysis of APE surfactants in the two Type IV deicer products in which they were identified. Results indicated that APE surfactants made up approximately 0.25–0.30 percent of deicer products K and I (Figure 3-10). The measured quantitative concentrations of individual APE EOs were consistent with the data of Table 3-7. Product K was dominated by OPE with a very low average EO number (3.6), indicating a relatively hydrophobic surfactant mixture, whereas product I was dominated by NPE, also having a relatively low (but broader) extent of ethoxylation (Figure 3-10).

Figure 3-10. Concentration (mg/L) of Individual APE Surfactant Ethoxymers (Ethoxy-Chain Lengths 1–17) in Product K and Product I (Type IV Deicers).



Values represent mean ± SD ($n = 3$). The total APE surfactant concentrations and average ethoxy-chain length (for octylphenol and nonylphenol ethoxylates) are presented for both deicer products.

Quantitative Analysis of Triazole-Based Corrosion Inhibitors Triazole-based organic corrosion inhibitors have been implicated previously in contributing to toxicity of deicer formulations (discussed in Section 2); therefore quantitative analyses of this compound class were performed in deicer products and pavement deicers (Table 3-8). Triazole-based corrosion inhibitors were not detected in any of the four Type I deicer products assayed by the TIE approach. However, benzotriazole and/or the two tolyltriazole isomers were detected and quantified in all four of the Type IV deicer products. The total triazole corrosion inhibitor concentration was highest in product K, consistent with the TIE results, where fraction 8 containing tolyltriazole was found to cause toxicity in the Microtox assay. The lack of observed toxicity in this fraction from other Type IV deicer products may have been due to the relatively lower total concentration of triazole compounds in these products. Traces of triazole corrosion inhibitors were detected in pavement deicer product L.

TABLE 3-8 Measured Concentrations (mg/L) of Triazoles in Deicer Products (mean ± SD; $n = 3$)

Deicer	Type	1H-BT	4-MeBT	5-MeBT	5,6-diMeBT
Product A	I	n/d	n/d	n/d	n/d
Product B	I	n/d	n/d	n/d	n/d
Product C	I	n/d	n/d	n/d	n/d
Product E	I	n/d	n/d	n/d	n/d
Product H	IV	218.8 ± 11.5	144.4 ± 5.9	237.2 ± 11.1	n/d
Product I	IV	n/d	56.4 ± 2.8	106.1 ± 5.3	n/d
Product J	IV	281.3 ± 16.5	n/d	n/d	n/d
Product K	IV	n/d	427.9 ± 14.8	731.7 ± 19.0	n/d
Product L	pavement	n/d	28.9 ± 1.4	62.2 ± 2.8	n/d
Product M	pavement		not assayed		
Product N	pavement		not assayed		

Analysis of Polymeric Thickeners in Type IV Deicer Products Chemical characterization of the polymeric thickeners was challenging, as these components were not amenable to routine chromatographic or mass spectrometric analyses (the molecular weights of polymeric thickeners are polydispersed and often greater than 1 MDa). Therefore, several spectroscopic techniques were employed to identify the chemical class of thickeners used in the Type IV deicer product formulations. Results of solid-state ATR-FTIR, H-NMR, and solid-state ^{13}C-NMR analyses indicated that products H, J, and K utilized polyacrylic acid (PAA) thickeners that gave ^{13}C-NMR spectra very similar to those of commercial Carbopol PAA materials. Spectra of thickener isolated from product I were unique and did not show similarity to the polymeric thickeners tested. The results of gravimetric quantitative analyses indicated that product H contained 0.347 ± 0.006 percent polymeric thickener, product I contained 0.270 ± 0.017 percent polymeric thickener, product J contained 0.677 ± 0.006 percent polymeric thickener, and product K contained 0.237 ± 0.006 percent polymeric thickener.

Validation of TIE Results *Toxicity Testing of Reformulated "Mock" Deicer Products* Resolution of the components responsible for observed toxicity in deicer products required a final stage of TIE testing; this was essentially a reverse TIE approach wherein mixtures were "built up" from identified and quantified components in order to verify that these components accounted for the full toxicity of the mixture from which they were originally isolated. This work served to validate the identity of our candidate toxicants identified through the TIE approach as described above. The approach taken was to utilize quantitative measurements (where available) of putative toxicants (identified through the TIE) as well as known major components of the deicer products to approximate the commercial product for toxicity testing. Because toxicity of Type IV deicer products was considerably greater than that of the Type I products tested and because TIE results from Type I products did not yield high-confidence leads on putative toxicants, our efforts in TIE validation were directed toward the four Type IV products tested.

Tables 3-9 through 3-12 present the results of toxicity testing for each Type IV deicer (H, I, J, and K) and its respective mock formulations, based on analytical data presented above. For each product, up to four mock formulations were prepared, with mock formulation 1 the simplest (containing water, FPD, and polymeric thickener), and mock formulation 4 the most complex (containing surfactants and corrosion inhibitors in addition to the components in mock 1). It should be noted that all components in mock formulations were closely matched for composition (e.g., FPD type and surfactant identity) to those identified from the respective products. In the case of Type IV products I and K, surfactant concentrations were quantified with high fidelity (see data above) and commercial sources for well-matched surfactant products were utilized. In these two cases (Type IV products I and K), the results of the mock deicer toxicity testing clearly indicated that APE surfactants were responsible for nearly all of the observed toxicity to *C. dubia* and fathead minnows (Tables 3-10 and 3-12), as only mock formulations containing the OPE and NPE surfactants resulted in significant toxicity, and this toxicity was well-matched to that of the commercial product (i.e., the mock fluids gave LC_{50} values very similar to those of the commercial deicers). In both cases, triazole-based corrosion inhibitors may have contributed slightly to the toxicity of mock fluids containing these components in the Microtox assay, consistent with previous reports for these compounds in deicers (Cancilla et al., 1997).

Reliable quantitation of the alcohol ethoxylate surfactants identified in toxic fractions from Type IV deicer products H and J was not possible given available analytical resources, as described above. A semiquantitative assay of these compounds was attempted using a colorimetric assay for nonionic surfactants standardized on an alcohol ethoxylate surfactant formulation that was qualitatively similar to those identified in products H and J (i.e. C_{12-14}EO 5-14). These results (and the standard alcohol ethoxylate surfactant formulation) were used to prepare mock formulations for products H and J and the resulting mock fluids were tested for toxicity. In both cases, full mock formulations (mock formulation 4 in Tables 3-9 and 3-11) resulted in no significant toxicity to aquatic species or Microtox, in contrast to the relatively high toxicity exerted by products H and J. It is very likely that the colorimetric assays used in the present work significantly underestimated the concentrations of alcohol ethoxylate surfactants present in these fluids. The concentrations obtained by this method for surfactants in products H and J were 0.09 g/L and 0.14 g/L respectively, both significantly lower than the surfactant concentrations measured in products I and K above (approximately 3.0 g/L). It was observed that high-quality calibrations were obtained for standard surfactants in the colorimetric assay; however, assay results from the commercial deicer formulations were not reproducible. We suspect that additional components present in the commercial deicer formulations (e.g. dyes and thickeners) introduced interferences in the analysis that were not present in the standards. Given these analytical problems with the colorimetric surfactant assay, we hypothesize that products H and J actually contain higher concentrations of alcohol ethoxylate surfactants than were measured here, and that these compounds were responsible for the toxicity observed for these commercial products. Evidence in support of this hypothesis is presented below.

Interestingly, results of mock formulation testing for all four Type IV deicer products indicated no significant contribution of polymeric thickener to toxicity. In the case of products I and K, all toxicity was explained by quantified surfactant concentrations, and in the case of products H and J, no significant toxicity was observed for the mock fluids even with quantitatively correct concentrations of thickener. These results suggest that the apparent toxicity of high molecular weight fractions and thickener fractions observed during the TIE process for Type IV deicers may have been due to imperfect separation of thickener from other components (e.g., surfactants) in the deicer fluid.

TABLE 3-9 Toxicity of Mock Type IV Deicer Product H to Aquatic Species

Formulation	**Water**	**Propylene Glycol (47 %)**	**Polyacrylic acid thickener (3.47 g/L)**	**Alcohol ethoxylate Surfactant (0.09 g/L)***	**1-H BT corrosion inhibitor (0.22 g/L)**	**4,5 MeBT corrosion inhibitor (0.38 g/L)**	**EC$_{50}$ and LC$_{50}$ Values (mg/L)**		
							Microtox	***C. dubia***	**Fathead Minnow**
Product H	✓	✓	✓	✓	✓	✓	474	948	2,666
Mock #4	✓	✓	✓	✓	✓	✓	6,619	>6,000	>6,000

Checkmark indicates presence of component in mock formulation.

*The surfactant used in this mock formulation was an aliphatic alcohol polyethoxylate formulation having C_{12-14} alkyl chain and a range of 5-14 ethoxylate units per molecule. This formulation was chosen as a good match to the alkyl- and polyethoxylate chain lengths of the alcohol ethoxylate surfactant used in the commercial product. The concentration of this surfactant in the commercial product was measured semiquantitatively using a colorimetric assay, and it is likely that the reported concentration (used in creating the mock fluid formulation) is much lower than the true concentration (see text for explanation)

TABLE 3-10 Toxicity of Mock Type IV Deicer Product I to Aquatic Species

Formulation	Water	Ethylene Glycol (59%)	Polyacrylic Acid Thickener (2.7 g/L)	NPEO Surfactant (3.0 g/L)	4,5 MeBT Corrosion Inhibitor (0.163 g/L)	EC_{50} and LC_{50} Values (mg/L)		
						Microtox	*C. dubia*	Fathead Minnow
Product I	✓	✓	✓	✓	✓	14,063	506	253
Mock #1	✓	✓	✓	—	—	>51,500	>3,000	>3,000
Mock #2	✓	✓	✓	✓	—	29,167	1,576	1,237
Mock #3	✓	✓	✓	—	✓	36,750	>3,140	>3,140
Mock #4	✓	✓	✓	✓	✓	7,737	725	290

Checkmark indicates presence of component in mock formulation.

TABLE 3-11 Toxicity of Mock Type IV Deicer Product J to Aquatic Species

Formulation	Water	Propylene Glycol (47%)	Polyacrylic Acid Thickener (6.7 g/L)	Alcohol Ethoxylate Surfactant (0.14 g/L)*	1-H BT Corrosion Inhibitor (0.28 g/L)	EC_{50} and LC_{50} Values (mg/L)		
						Microtox	*C. dubia*	Fathead Minnow
Product J	✓	✓	✓	✓	✓	338	528	1,041
Mock #4	✓	✓	✓	✓	✓	8,538	>3,000	>3,000

Check mark indicates presence of component in mock formulation.
*The surfactant used in this mock formulation was an aliphatic alcohol polyethoxylate formulation having $C_{12\text{-}14}$ alkyl chain and a range of 5-14 ethoxylate units per molecule. This formulation was chosen as a good match to the alkyl- and polyethoxylate chain lengths of the alcohol ethoxylate surfactant used in the commercial product. The concentration of this surfactant in the commercial product was measured semiquantitatively using a colorimetric assay, and it is likely that the reported concentration (used in creating the mock fluid formulation) is much lower than the true concentration (see text for explanation).

TABLE 3-12 Toxicity of Mock Type IV Deicer Product K to Aquatic Species

						EC$_{50}$ and LC$_{50}$ Values (mg/L)		
Formulation	**Water**	**Propylene Glycol (46.6%)**	**Polyacrylic Acid Thickener (2.37 g/L)**	**OPEO Surfactant (3.0 g/L)**	**4,5 MeBT Corrosion Inhibitor (1.16 g/L)**	**Microtox**	***C. dubia***	**Fathead Minnow**
Product K	✓	✓	✓	✓	✓	2,620	2,600	888
Mock #1	✓	✓	✓	—	—	>11,160	>11,160	>11,160
Mock #2	✓	✓	✓	✓	—	2,807	1,452	1,140
Mock #3	✓	✓	✓	—	✓	4,313	>11,500	>11,500
Mock #4	✓	✓	✓	✓	✓	2,250	1,061	576

Checkmark indicates presence of component in mock formulation.

Toxicity Testing of Individual Putative Toxicants We conducted further validation of the results of our TIE assays by testing toxicity of individual components that had been identified from Type IV deicers as putative toxicants. Specifically, we tested the toxicity of a representative polyacrylic acid thickener, representative NPE and OPE surfactants, and that of two alcohol ethoxylate surfactant formulations that had very similar chemical composition (e.g. alkyl chain and ethoxy chain lengths) to the surfactants identified from Type IV deicers H and J. Specifically, the $C_{12\text{-}14}$EO 5-14 surfactant was an excellent match in both chromatographic retention time and mass spectral intensities of component peaks to the alcohol ethoxylate surfactants identified in deicers H and J. Accordingly, this surfactant was chosen for inclusion in mock deicer fluids for toxicity testing (results above). Results of the polyacrylic acid toxicity assay indicate that this material (tested as a 2.5 g/L solution in triethanolamine-buffered aqueous solution) is relatively non-toxic (Table 3-13), exerting toxicity at values far higher than those obtained for the four Type IV deicer products (which had similar concentrations of polymeric thickener in formulation).

TABLE 3-13 Toxicity of Selected Deicer Components Used in Mock Formulations

	EC$_{50}$ and LC$_{50}$ Values (mg/L)		
Component	**Microtox**	***C. dubia***	**Fathead Minnow**
Polyacrylic acid thickener (100%)	807	45.8	140
Nonylphenol ethoxylate surfactant	13.0	2.23	1.21
Octylphenol ethoxylate surfactant	16.1	2.92	1.41
$C_{12\text{-}14}$EO 5-14 alcohol ethoxylate surfactant	4.99	1.45	1.98
$C_{14\text{-}15}$EO 5-25 alcohol ethoxylate surfactant	1.22	0.44	1.08

TABLE 3-13 Toxicity of Selected Deicer Components Used in Mock Formulations

Component	EC$_{50}$ and LC$_{50}$ Values (mg/L)		
	Microtox	*C. dubia*	Fathead Minnow
5 MeBT*	4.25	81.3	22.0
4,5 MeBT*	6.08	80.7	30.1

* Previously published data (Corsi, et al. 2006a).

The two alkylphenol ethoxylate surfactant formulations exhibited toxicity at levels relevant to concentrations detected in deicers (Table 3-13). Considering these toxicity values along with concentrations detected in Type IV formulations, a substantial amount of the toxicity in Type IV formulations K and I can be attributed to alkylphenol ethoxylate surfactants.

The two alcohol ethoxylate surfactant formulations tested showed high toxicity to all species (Table 3-13). Assuming that alcohol ethoxylate surfactants were used in the Type IV deicer products H and J at concentrations approaching those of APE surfactants in products I and K (~3.0 g/L), the expected EC$_{50}$/LC$_{50}$ values for the formulated products would be approximately 400–1,600 mg/L (Microtox), 150–480 mg/L (*C. dubia*), and 360–660 mg/L (fathead minnow). These estimates are quantitatively very similar to the toxicity values obtained for Type IV deicer products H and J (Tables 3-9 and 3-11). Because the alcohol ethoxylate surfactants present in deicer products H and J must be present in sufficient concentration to be effective at reducing fluid surface tension, and because these surfactants likely have very similar activity to that of the APE surfactants used in products I and K, the assumption that alcohol ethoxylate surfactants were present in deicers H and J at higher-than-measured concentrations is reasonable. In addition, the TIE data for deicers H and J indicated that alcohol ethoxylate surfactants were the major chemical components of the fractions contributing to aquatic toxicity. Taken together, these results support the hypothesis that alcohol ethoxylates may have been primarily responsible for the toxicity of these two Type IV deicer products.

Benzotriazole derived corrosion inhibitors were detected in the Type IV deicers at concentrations relevant to toxicity values primarily in the Microtox testing based on previously published toxicity information (Table 3-13).

Discussion and Synthesis of Results

The overall results of the toxicity, TIE, targeted analysis, and reverse-TIE work conducted on deicer products to date can be summarized in the following points:

1. Type IV deicer products were significantly more toxic to aquatic organisms than were either Type I deicer or pavement deicer products.
2. Toxicity of pavement deicer products is associated primarily with freezing-point depressants.
3. Toxicity in fractionated Type IV and Type I deicer products was associated predominantly with the presence of nonionic surfactants of the polyethoxylated type. Toxic fractions contained not only APE surfactants but also aliphatic alcohol ethoxylate

surfactants. In one case, relatively high concentrations of triazole-based corrosion inhibitors in a Type IV deicer triggered toxicity in TIE assays.

4. Toxicity testing of reformulated, "mock" Type IV deicers and putative toxicants identified through the TIE verified the contribution of surfactants to the toxicity of these deicers and discounted the contribution of polymeric thickeners to this toxicity.

During the course of the toxicity, TIE, and analytical measurement work described herein, several challenges arose that complicated interpretation of the data. First, it was difficult to achieve highly reproducible isolation of all components during fractionation while retaining the full toxicity of the neat deicer products. Loss of toxicity during fractionation was a pervasive issue throughout the TIE work. Nevertheless, based on the data obtained to date, many of the compounds that likely contributed most to deicer toxicity have been identified. This is particularly the case with the more toxic Type IV deicer products. It should be noted that there exists the possibility that observed reductions in toxicity of deicer products after chemical fractionation may have been due to synergistic toxic effects among individual components in these complex mixtures. That is, the toxicity of the formulated deicers may have, in fact, been greater than the additive sum of toxicities of individual components tested in isolation. There is precedence for such synergistic toxicity – a good (and relevant) example is the enhanced efficacy of some organic pesticide compounds toward target insects when they are applied to crops in combination with a surfactant "inert" (which is often a polyethoxylated nonionic surfactant (Krogh et al., 2003).

The implications of the findings reported here include the need to carefully consider choice of surfactants in formulating deicer products. It is important to note that although much attention has been focused on APE surfactants with respect to their potential to resist degradation through treatment and persist in the environment after release (potentially causing a longer-term toxicity hazard), the alcohol ethoxylate surfactants seem to contribute similar toxicity to the deicer formulations as the APEs. It is thus clear that one must consider toxicity of formulated deicer products differently from that of products after wastewater treatment or environmental degradation—it is most likely *after* release that differences in toxicity profiles between aliphatic alcohol polyethoxylate surfactants and APE will become manifest. This underlines the importance of considering environmental fate of surfactant candidates when formulating deicer products. In particular, within the class of alcohol polyethoxylate surfactants it will be necessary to consider the choice between linear alcohol hydrophobes (highly biodegradable) and branched (secondary) alcohol hydrophobes (resistant to degradation). Interestingly, such choices may have little impact on the toxicity of deicer products tested directly, but may significantly impact the potential for release of deicer products post-use to cause toxic effects in the aquatic environment.

One point of caution that must be considered is that deicer manufacturers are constantly conducting research to develop improved deicer products. Four manufacturers introduced new Type IV formulations to be available in the 2007–2008 winter season. These AAF formulations were not included in this study. In addition, it is expected that deicer formulations will continue to change in the future including substitutions for additives that have been identified here as sources of toxicity in formulations.

Biochemical Oxygen Demand

Introduction

The potential for aircraft and airfield deicing runoff to contribute to decreased DO in receiving waters is a function of the biodegradable materials in the deicers in stormwater discharges, and the characteristics of the receiving waters, which affect the rate at which biodegradation occurs. Biochemical oxygen demand (BOD) content describes the magnitude of biodegradable materials in a product, while the speed at which those materials are actually biodegraded is reflected in the degradation rate. These characteristics can counterbalance each other. For example, one product may have a higher ultimate BOD (i.e., BOD_{ult}) than another, but if it degrades at a slower rate than the lower BOD product, the impacts on oxygen depletion in receiving water may actually be less because the BOD exertion is spread out over a significantly longer time. Thus, characterizing the BOD content of deicers and how that content is exerted under ambient conditions is central to understanding the actual implications of discharges at any given facility. For the same reasons, these characteristics are key in establishing a benchmark against which alternative formulations can be evaluated.

The technical approach to characterizing the potential for D.O. impacts was designed around the accurate measurement of BOD expressed over a range of time periods and under both the standard test temperature (20°C) and a representative ambient wintertime temperature (5°C). Because some airports discharge to marine and estuarine waters, both freshwater and marine tests were conducted. The testing was designed to produce estimates of classic BOD content measurements (e.g., BOD_5, BOD_{ult}) and characterizations of rates of biodegradation. Standard testing of BOD_5 was conducted as a reference to traditionally measured values. In addition, time-series tests were conducted using a modification of the standard methods, using larger volume bottles to deal with the high oxygen demand found in aircraft and airfield deicers. The chemical oxygen demand (COD) of each formulation was measured to estimate BOD_{ult}.

Methods

Analyses were conducted on four aircraft and three pavement deicer formulations, representative of the categories of deicers commonly used. COD analyses were performed according to American Society of Testing and Materials method D1252-88(B).

Traditional 5-day BOD analyses were performed in triplicate according to *Standard Methods for the Examination of Water and Wastewater*, method 5210B (American Public Health Association et al., 1995).

The biodegradability of the deicer formulations was characterized in terms of oxygen demand exerted over time at 20°C and 5°C in fresh water and artificial seawater using a modification to method 5210B. Specifically, time-series BOD analyses were performed using 2,120-mL custom BOD bottles rather than the traditional 300-mL bottles. Single dilutions were prepared based on the results of the COD and conventional BOD_5 analyses, and the D.O. was monitored at 5, 15, 28, and 40 days. As D.O. concentrations approached 2.0 mg/L, the samples were re-aerated using filtered compressed air and then returned to the incubator. Laboratory blanks were tested along with the samples to correct for the contribution of the "seed" material (i.e., source of microorganisms) and any demand exerted by the reagent water used to prepare the samples. Five replicate glucose-glutamic acid controls were also tested in fresh water at 20°C and 5°C. Results were considered valid as long as 2 mg or more of oxygen depletion was observed in test vials at each measurement interval during the test. Measurement uncertainty was considered to be too large for accurate reporting with less than 2 mg of oxygen demand exerted over the time interval.

Seawater BOD analyses were prepared under the general guidelines of International Standards Organization (ISO) method 16221. A seawater BOD seed inoculum was prepared from a suspension of estuarine sediment collected near Kiawhah Island, South Carolina, and artificial seawater. An aliquot of the inoculum was added to each of the BOD bottles prior to incubation to ensure that adequate organisms were present to drive the BOD test. Heterotrophic plate counts were performed on aliquots from the 40-day 20°C and 5°C BOD samples to confirm that adequate microbial populations were present to conduct the test. At least 10^5 organisms per mL were found, confirming adequate presence of organisms during the test period.

The 40-day BOD test is a cost-effective, efficient, and practical approach to estimating ultimate BOD. The liquid and solid deicer products tested in this study were "neat" products and devoid of ammonia or other combined nitrogen compounds that could contribute to nitrification. Any minimal nitrification that may have occurred during the 40-day test period would be eliminated through blank correction. Consequently, only total BOD measurements were made, with the assumption that they would be essentially equivalent to carbonaceous BOD (i.e., oxygen demand for carbon source only). The effectiveness of the 40-day BOD as an estimate of ultimate BOD can be evaluated by comparing it to the corresponding COD.

Seed Inoculums

Freshwater and seawater seed inoculums were prepared using primary wastewater from Madison (Wis.) Metropolitan Sewerage District and marine sediment from South Carolina. Several attempts were made to acclimate these seeds to two mixtures of deicer products to better approximate receiving water conditions. One acclimation mixture contained four aircraft deicers and the other mixture contained three pavement deicers. Acclimation of the seed organisms was monitored with heterotrophic plate counts using standard and marine agars. Organism numbers in both inoculums decreased over the six-day test period indicating that they did not acclimate to the deicer mixtures. The implications of this observation are primarily to rates of initial degradation, as discussed below.

The BOD rate is primarily controlled by temperature, and number and types of organism present. Theoretically, if temperature is controlled (i.e., 20–25°C) and the inoculums are fed the deicer mixtures (a carbon or food source) and essential nutrients, a population of organisms acclimated or adapted to the deicers should flourish. Ideally, acclimated seed will provide a faster biochemical stabilization of the deicer products during the 40-day test period. Use of unacclimated seed inoculums will generally not affect the outcome of the 40-day test. It will typically result only in a slightly longer initial lag period until the organism population acclimates to the food source and grows.

Developing seed inoculums is typically done on a trial-and-error basis by attempting to find the ideal food (carbon)-to-organism ratio. This can be a difficult and time-consuming process. Typically, when an acclimated inoculum is prepared, a lag phase will be observed followed by an exponential growth phase as the organisms adapt to the food source. However, this was not observed in these tests. The lack of growth in the seed inoculums may have been caused by a less than ideal carbon-to-organism ratio. Another consideration is that the carbon sources were made up of multiple deicer products. The sodium formate PDM product showed inhibitory affects in both the 5- and 40-day BOD tests. This product likely had an inhibitory affect on the seed inoculums as well. Due to time constraints, further seed acclimation trials were discontinued with the understanding that there may be a slightly longer lag in test period. However, the quality of final test results was not expected to be compromised. Consequently, the 40-day BOD tests were prepared using primary wastewater from the Madison Metropolitan Sewerage District and marine sediment from South Carolina as the inocula for the freshwater and marine tests, respectively. Heterotrophic plate counts done at critical times during the 40-day test period showed that at least 10^5 microorganisms per milliliter were present, which is consistent with ISO 16221 guidelines for biodegradability studies.

Results

The results of the traditional BOD_5 and COD tests are presented in Table 3-14. Measurements are expressed in terms of mass (mg/kg) as well as concentration (mg/L). The specific gravity (s.g.) of each product is shown to explain the basis for the conversion between the two (i.e., mg/L = mg/kg ÷ s.g.). Results of the time series BOD analyses are presented in Table 3-15.

TABLE 3-14 COD and BOD$_5$ for Selected Aircraft and Airfield Deicers and Anti-icers

			COD		BOD$_5$		Values Expressed as Primary Source of Oxygen Demand		
Formulation	% FPD	Specific Gravity	mg/kg % RSD (Replicates)	mg/L	mg/kg % RSD (3 Replicates)	mg/L	Primary Source	COD (mg/kg)	BOD$_5$ (mg/kg)
EG Type I	92	1.1	1,180,000 0.06 (3)	1,050,000	492,000 6.35	439,00	Ethylene glycol	1,280,000	535,000
EG Type IV	64	1.1	826,000 5.50 (3)	772,000	331,000 7.74	309,000	Ethylene glycol	1,290,000	517,000
PG Type I	88	1.04	1,420,000 1.29 (3)	1,380,000	990,000 0.70	961,000	Propylene glycol	1,610,000	1,130,000
PG Type IV	50	1.06	842,000 1.32 (3)	818,000	539,000 2.47	523,000	Propylene glycol	1,680,000	1,080,000
Potassium acetate (liquid)	50	1.28	315,000 1.86 (3)	250,000	247,000 0.73	196,000	Acetate	1,050,000	821,000
Sodium acetate (solid)	96	na	700,000 0.38 (4)	na	571,000 0.48	na	Acetate	1,010,000	826,000
Sodium formate (solid)	98	na	242,000 2.14 (4)	na	--[a]	na	Formate	373,000	--[a]

[a] BOD$_5$ 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.

TABLE 3-15 Biodegradation of Aircraft and Pavement Deicers and Anti-icers at 20°C and 5°C with Measurements at 5, 15, 28, and 40 Days

		Freshwater 20°C		**Marine Water 20°C**		**Freshwater 5°C**		**Marine Water 5°C**	
Formulation	**Day**	**Mean (mg/kg)**	**% RSD**	**Mean (mg/kg)**	**% RSD**	**Mean (mg/kg)**	**% RSD**	**Mean (mg/kg)**	**% RSD**
EG Type I	5	260,000	17	—	—	ND[a]	100	—	—
	15	802,000	2.3	—	—	ND[a]	35	—	—
	28	832,000	4.8	—	—	184,000	17	—	—
	40	921,000	2.5	—	—	645,000	3.7	—	—
EG Type IV	5	196,000	19	—	—	ND[a]	0	—	—
	15	570,000	1.8	—	—	ND[a]	81	—	—
	28	618,000	1.5	—	—	ND[a]	14	—	—
	40	687,000	2.0	—	—	190,000	9.4	—	—
PG Type I	5	842,000	4.3	344,000	18	ND[a]	21	ND[a]	45
	15	1,120,000	3.5	1,140,000	1.5	299,000	10	ND[a]	33
	28	1,160,000	2.7	1,240,000	2.2	836,000	3.9	ND[a]	168
	40	1,260,000	2.5	1,280,000	3.3	868,000	3.2	<183,000[a]	114
PG Type IV	5	492,000	0.6	148,000	114	ND[a]	110	ND[a]	74
	15	640,000	0.8	626,000	11	ND[a]	11	ND[a]	60
	28	659,000	4.5	704,000	5.4	494,000	5.7	ND[a]	92
	40	717,000	1.0	723,000	4.1	609,000	2.8	<281,000[a]	176
Potassium acetate deicer	5	260,000	8.7	225,000	2.3	96,300	16	ND[a]	33
	15	306,000	9.8	284,000	1.4	243,000	4.8	ND[a]	63
	28	292,000	5.3	297,000	1.3	269,000	5.0	221,000	3.9
	40	299,000	7.2	374,000	14	270,000	4.9	219,000	13

TABLE 3-15 Biodegradation of Aircraft and Pavement Deicers and Anti-icers at 20°C and 5°C with Measurements at 5, 15, 28, and 40 Days

		Freshwater 20°C		Marine Water 20°C		Freshwater 5°C		Marine Water 5°C	
Formulation	**Day**	**Mean (mg/kg)**	**% RSD**	**Mean (mg/kg)**	**% RSD**	**Mean (mg/kg)**	**% RSD**	**Mean (mg/kg)**	**% RSD**
Sodium acetate deicer	5	ND[a]	21	—	—	436,000	2.2	—	—
	15	731,000	1.8	—	—	551,000	2.8	—	—
	28	678,000	1.6	—	—	633,000	1.2	—	—
	40	698,000	1.7	—	—	655,000	1.2	—	—
Sodium formate deicer[b]	5	ND[a,b]	11	—	—	ND[a,b]	131	—	—
	15	—[b]	0.5	—	—	ND[a,b]	32	—	—
	28	—[b]	4.4	—	—	ND[a,b]	31	—	—
	40	—[b]	3.7	—	—	—[b]	30	—	—

— Analyses not included in this study.

[a] Did not meet oxygen depletion criteria for reporting.

[b] 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.

COD test results estimate the potential TOD for each of the liquid and solid deicer formulations. These results, as well as results from standard BOD_5 and the 40-day BOD series testing, show wide variability among the tested products (Tables 3-14 and 3-15). This variability is the result of both differences in the BOD of the FPDs, and the concentration of the FPDs in each product. For the aircraft deicers and anti-icers, PG and EG are the primary sources of oxygen demand. For the PDMs, acetate and formate are the primary sources of oxygen demand. To normalize the results for the varying concentrations of these FPDs in the tested products, oxygen demand was computed "as primary source" (i.e., as PG, as EG, as acetate, or as formate) for COD and BOD_5 (Table 3-14) and for the 40-day BOD series (Table 3-16) for each product. Presenting the data in this form allows for direct comparison of the same FPD in different formulations. Results from the two EG formulations are comparable, as are results from the two PG formulations and results from the two acetate-based formulations. Definition of BOD and COD for the primary sources allows for an evaluation of the sources of COD and BOD in individual airport runoff samples, or construction of a "mass balance" of oxygen demand.

Comparison of Traditional 5-Day BOD and 40-Day BOD Traditional BOD test results (Table 3-14) from each of the aircraft and pavement deicers agreed well with those published in the manufacturers' product literature. Comparison of the results from the traditional BOD_5 analyses with the day 5 results from the 40-day tests (Table 3-15) showed generally lower results using the modified BOD test methodology (Figure 3-11). This difference appears to be the result of less than optimal food-to-organism ratios in the modified test method. The traditional test is carried out in standard 300-mL bottles at 20°C using multiple sample dilutions, generally five or six. Because the 300-mL BOD bottles are small and water can contain only a finite amount of D.O., it is necessary to prepare multiple dilutions to satisfy the test criteria of an oxygen depletion of at least 2 mg/L of D.O. in 5 days while maintaining a residual D.O. concentration of at least 1 mg/L. The goal is to find the ideal carbon (food)-to-organism ratio in at least two of the five or six dilutions. In contrast to that approach, the 40-day tests are conducted in special 2,120-mL BOD bottles. Because the bottles are large, D.O. measurements are made on a more regular basis, and aeration is provided to ensure adequate D.O. throughout the test, only one dilution is prepared. There tends to be more of a lag time while the population of organisms grows to achieve the ideal carbon-to-organism ratio. Consequently, the day 5 results in the 2,120-mL bottles tend to be slightly lower than that observed in the traditional BOD test.

Formulation Biodegradability Comparison of COD and BOD_5 results provides an indication of the biodegradability of each product in 5-day laboratory tests (Table 3-14, Figure 3-12). The COD test is used to measure the organic matter of a sample that is susceptible to breakdown by a strong chemical oxidant. The COD result is not exactly the same as an ultimate BOD because ultimate BOD reflects biological activity not that of a strong chemical oxidant. However, oxidation of most organic compounds is 95 to 100 percent of theoretical value, and the COD results provide a valuable tool in interpreting the BOD data from the products. By looking at percent degradation ([BOD/COD] × 100), relative comparisons can be made of how fast BOD is exerted among deicer products.

TABLE 3-16 Biodegradation of Aircraft and Pavement Deicers and Anti-icers at 20°C and 5°C with Measurements at 5, 15, 28, and 40 Days Presented as Concentration of Primary Source of Oxygen Demand

Formulation	Day	Mean BOD (mg/kg) Freshwater 20°C	Marine Water 20°C	Freshwater 5°C	Marine Water 5°C
EG Type I (as ethylene glycol)	5	283,000	—	ND[a]	—
	15	871,000	—	ND[a]	—
	28	904,000	—	200,000	—
	40	1,000,000	—	702,000	—
EG Type IV (as ethylene glycol)	5	306,000	—	ND[a]	—
	15	891,000	—	ND[a]	—
	28	966,000	—	ND[a]	—
	40	1,070,000	—	297,000	—
PG Type I (as propylene glycol)	5	957,000	391,000	ND[a]	ND[a]
	15	1,270,000	1,300,000	340,000	ND[a]
	28	1,320,000	1,410,000	950,000	ND[a]
	40	1,430,000	1,460,000	986,000	<208,000[a]
PG Type IV (as propylene glycol)	5	984,000	296,000	ND[a]	ND[a]
	15	1,280,000	1,250,000	ND[a]	ND[a]
	28	1,320,000	1,410,000	988,000	ND[a]
	40	1,430,000	1,450,000	1,220,000	<562,000[a]
Potassium acetate deicer (as acetate)	5	864,000	748,000	320,000	ND[a]
	15	1,020,000	944,000	807,000	ND[a]

TABLE 3-16 Biodegradation of Aircraft and Pavement Deicers and Anti-icers at 20°C and 5°C with Measurements at 5, 15, 28, and 40 Days Presented as Concentration of Primary Source of Oxygen Demand

		Mean BOD (mg/kg)			
Formulation	**Day**	**Freshwater 20°C**	**Marine Water 20°C**	**Freshwater 5°C**	**Marine Water 5°C**
	28	970,000	987,000	894,000	721,000
	40	993,000	1,240,000	897,000	718,000
Sodium acetate deicer (as acetate)	5	ND[a]	—	631,000	—
	15	1,060,000	—	797,000	—
	28	981,000	—	916,000	—
	40	1,010,000	—	948,000	—
Sodium formate deicer[b] (as formate)	5	ND[a,b]	—	ND[a,b]	—
	15	—[b]	—	ND[a,b]	—
	28	—[b]	—	ND[a,b]	—
	40	—[b]	—	—[b]	—

— Analyses not included in this study.

[a] Did not meet oxygen depletion criteria for reporting.

[b] 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.

Figure 3-11. Comparison of 5-day BOD results obtained using the traditional BOD5 and modified 40-day time-series methods. Error bars represent 95 percent confidence intervals.

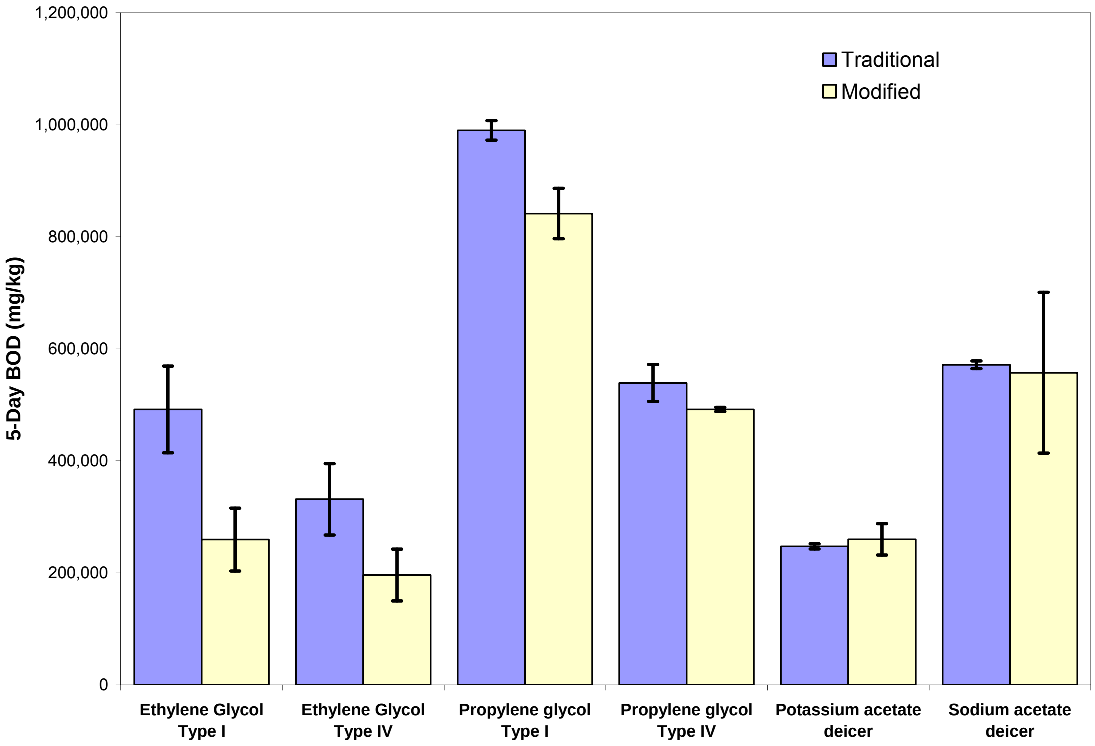
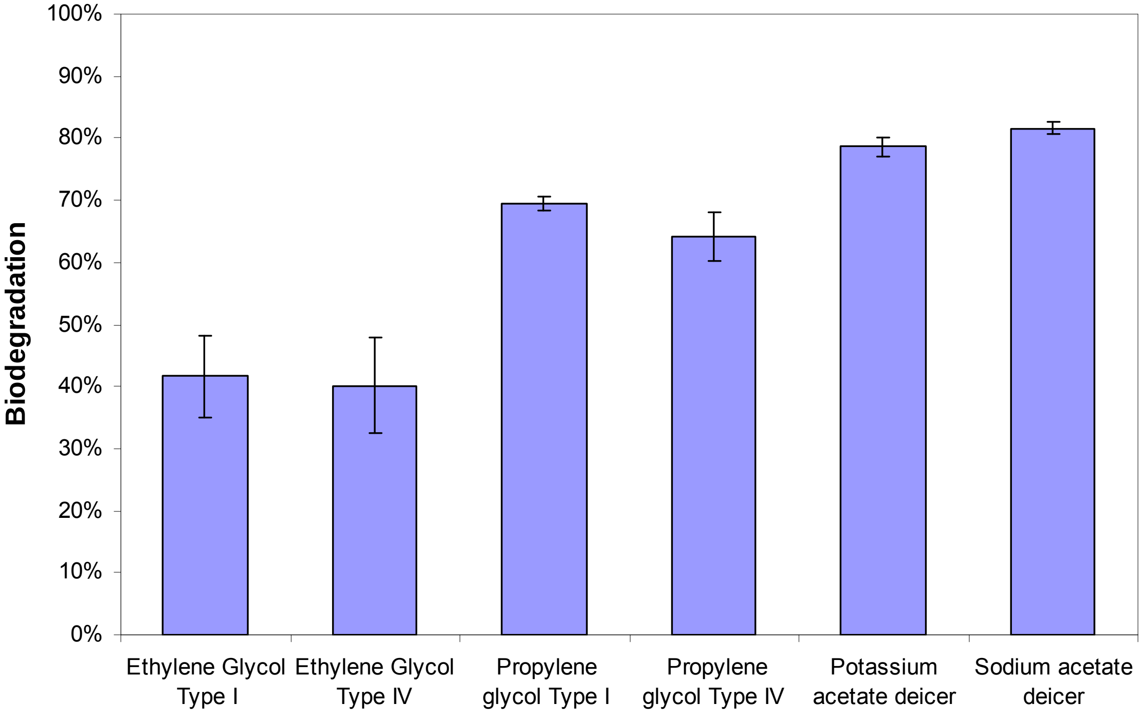


Figure 3-12. Percent biodegradation of selected aircraft and airfield deicers and anti-icers based on 5-Day BOD-to-COD ratios. Error bars represent 95 percent confidence intervals.



Biodegradability is important because the rate at which BOD is exerted affects the impact of BOD discharges on receiving water DO. For a given BOD_{ult} and a fixed set of discharge conditions, a slower rate of degradation will have a reduced impact on receiving water DO because the balance between the rates of DO consumption (i.e., BOD exertion) and reaeration processes that replenish DO will be more advantageous. Under certain conditions, a formulation with a higher BOD_{ult} but slower rate of biodegradation could have a lesser impact on receiving water DO than a formulation with a lower BOD_{ult} but faster rate of biodegradation.

Traditional BOD_5 results yielded biodegradability values of between 40 percent and 79 percent. As is discussed below, there is strong reason to believe that inhibitory effects from the sodium formate formulation are responsible for a very low observed percent biodegradation and so is not included in these data. A similar comparison of 40-day BOD to COD results at 20°C for freshwater and marine-water tests resulted in 78 percent to greater than 100 percent degradation (Figures 3-13 and 3-14). Calculated biodegradation greater than 100 percent reflects measurement error inherent in the analytical methods. The only notable difference between fresh- and marine-water results was on the fifth day of the 40-day tests. Marine-water tests exerted less oxygen demand through the fifth day than that in freshwater tests, but results beyond 5 days were comparable.

Figure 3-13. Percent biodegradation of selected aircraft and airfield deicers and anti-icers at 20°C in freshwater based on a 40-day BOD time series as compared to COD values. Error bars represent 95 percent confidence intervals.

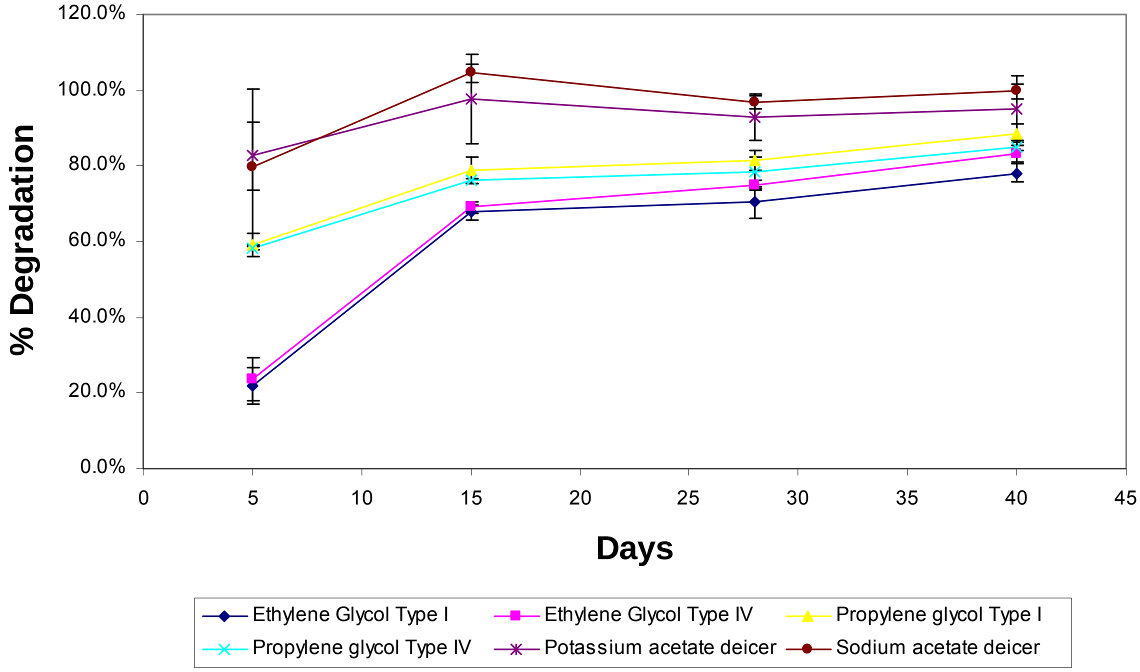
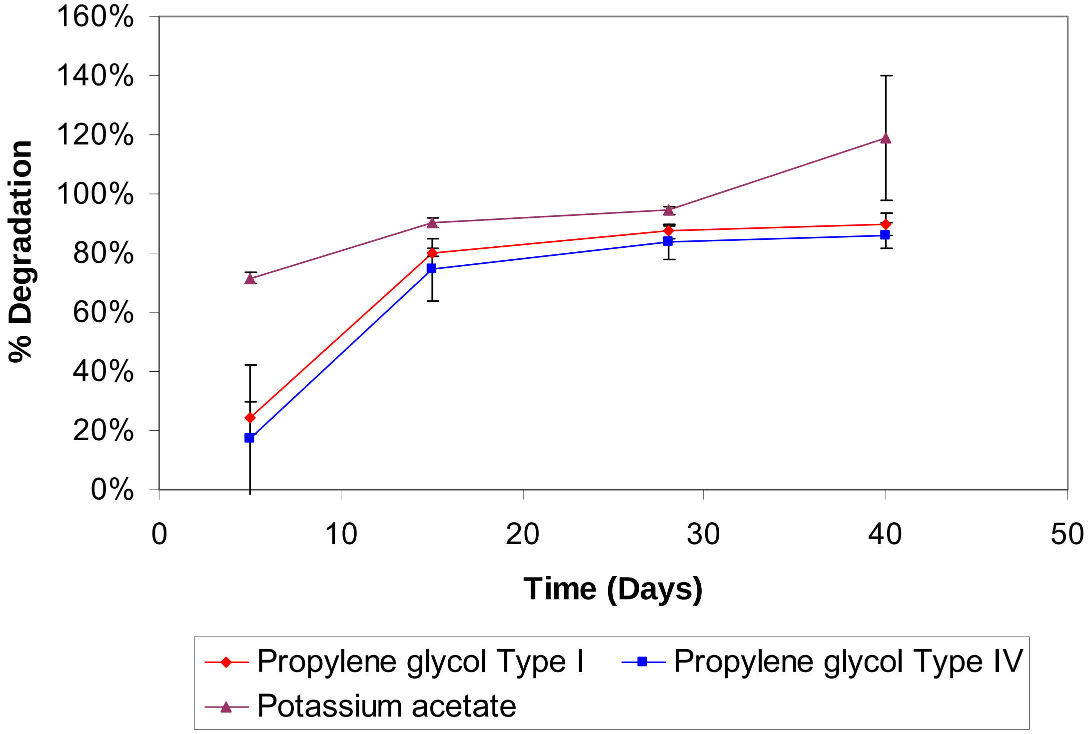
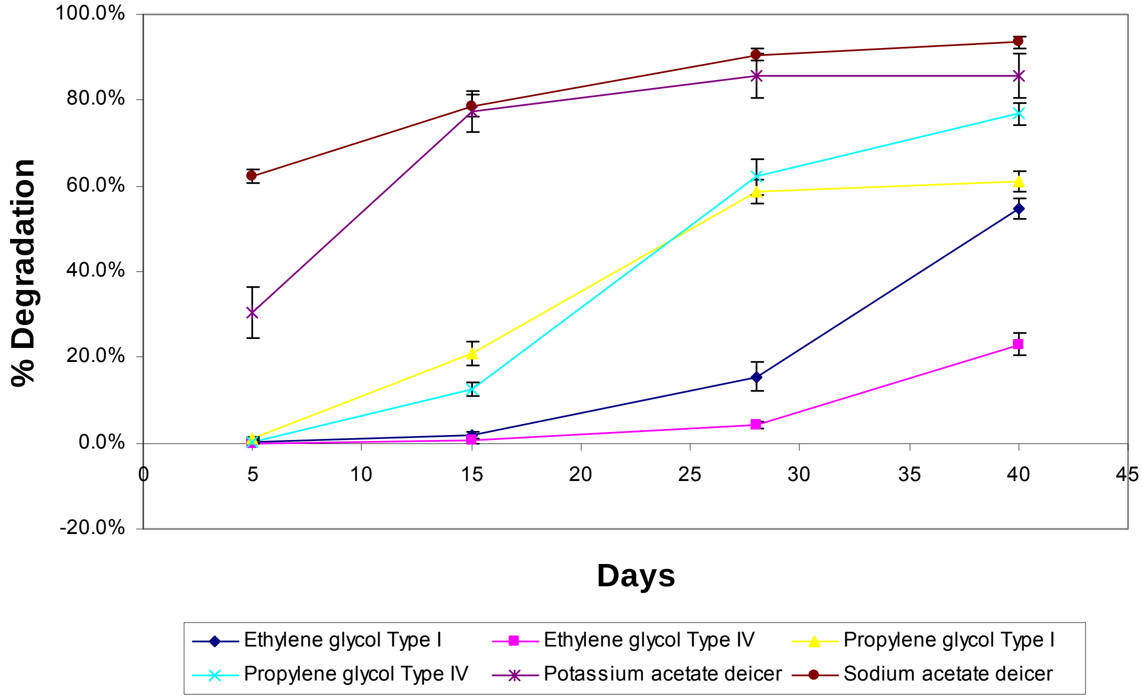


Figure 3-14. Percent biodegradation of selected aircraft and airfield deicers and anti-icers at 20°C in marine water based on a 40-day BOD time series as compared to COD values. Error bars represent 95 percent confidence intervals.



Results of the 40-day freshwater tests at 5°C (Figure 3-15) indicate 23–55 percent degradation for EG products, 61–77 percent degradation for PG products, 86 percent for the potassium acetate product, and 94 percent for the sodium acetate product. In general, the acetates degraded fastest, whereas the rates of degradation of the PG-based fluids were slower, and those of the EG-based products were slower still. The sodium formate deicer showed no significant degradation over the period of the test, presumably due to toxicity to the seed organisms.

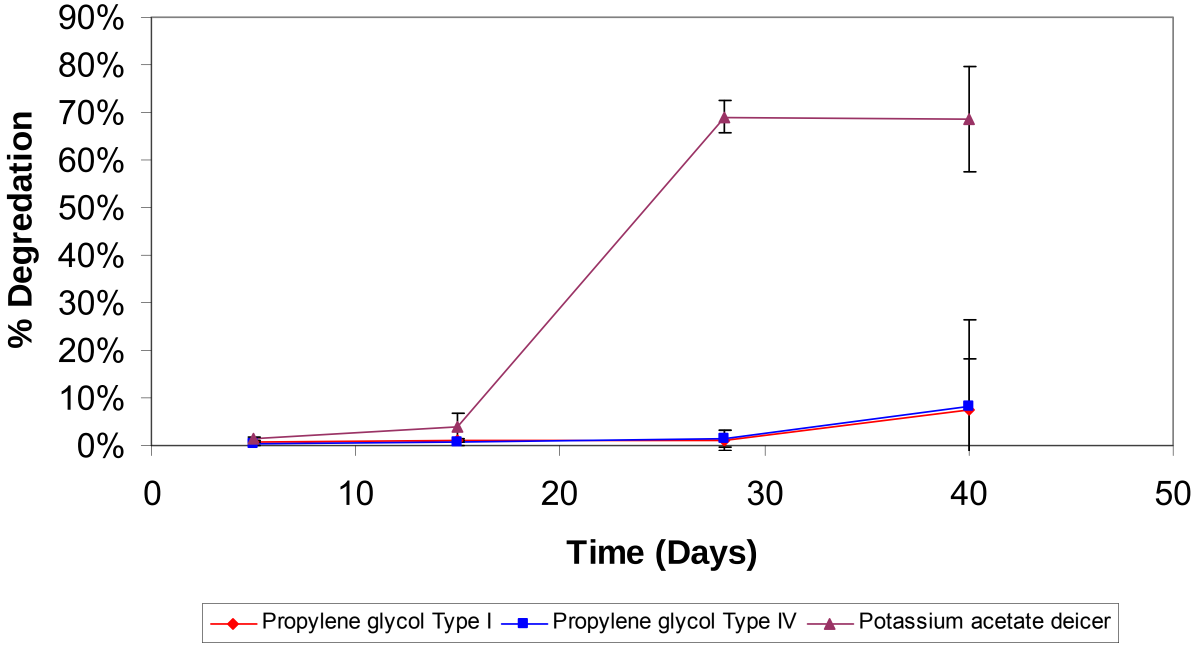
Figure 3-15. Percent biodegradation of selected aircraft and airfield deicers and anti-icers at 5°C in freshwater based on a 40-day BOD time series as compared to COD values. Error bars represent 95 percent confidence intervals.



Results of the 40-day marine-water tests at 5°C (Figure 3-16) indicate that PG formulations degraded less than 10 percent during the test period, whereas the potassium acetate liquid PDM degraded by 69 percent.

Comparison of 5°C test results with the 20°C test results in both fresh water and marine water indicate that the lower temperature significantly reduced the rate of BOD exertion. Heterotrophic plate counts were similar in 5°C and 20°C tests, so it can be concluded that lower BOD results reflect reduced biological activity in the lower temperature tests. Although an exact comparison to low-temperature environmental response is not possible, it is reasonable to conclude that biological response in waters receiving airport deicing discharges would also be significantly reduced at low temperatures. Quantification of such in situ reductions, however, cannot be estimated with available data because of the differences between laboratory and field conditions, which are site-specific.

Figure 3-16. Percent biodegradation of selected aircraft and airfield deicers and anti-icers at 5°C in marine water based on a 40-day BOD time series as compared to COD values. Error bars represent 95 percent confidence intervals.



The sodium formate solid runway deicer exhibited an apparent inhibitory affect on microorganisms during BOD testing. This effect is often referred to as a "sliding" BOD, characterized by a decrease in observed BOD with increasing sample concentration (Figure 3-17). As sample concentration increases, so does the constituent that inhibits the microbial activity (Stover and McCartney, 1984). The 40-day BOD tests showed biodegradability of the sodium formate solid runway deicer was only 26 percent in 20°C tests and not detectable in 5°C tests, also indicating an inhibitory effect. Microtox test results show the formulated product exhibiting greater toxicity than that of the sodium formate alone, indicating toxicity to microorganisms. Combined results of BOD, COD, and Microtox testing indicate that an additive component of this particular formulation has toxicity to microorganisms, resulting in inhibition of oxygen demand.

Relative BOD decay rates were estimated with a nonlinear regression technique using the following simple first-order decay model:

$$\mathrm{BOD}_t = \mathrm{BOD}_{\mathrm{ul}t} \times (1 - e^{-kt})$$

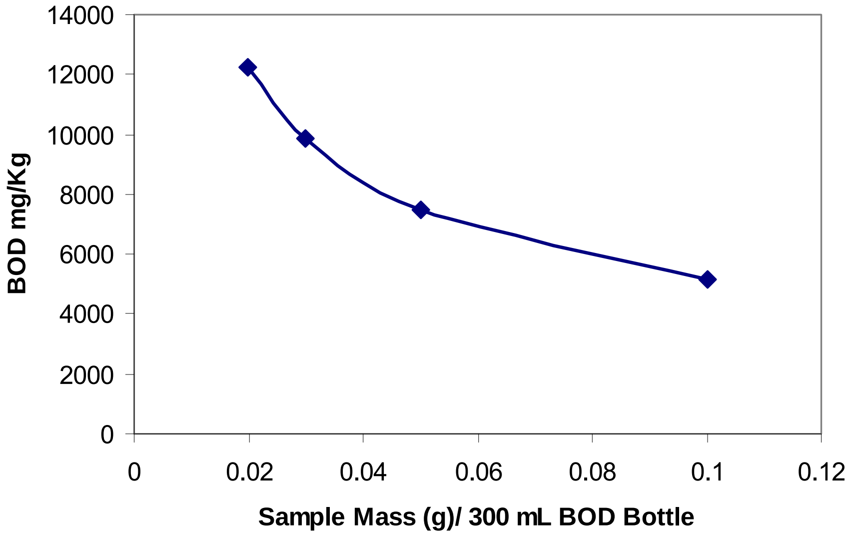
Where:

BOD_t = BOD exerted at time t (mg/L)

$\mathrm{BOD}_{\mathrm{ul}t}$ = Ultimate BOD (mg/L)

k = First-order decay rate (day^{-1})

Figure 3-17. Inhibitory effect of sodium formate deicer on the BOD_5 test results.



Rates were estimated for those formulations that had acceptable BOD from day 5 to day 40 (Table 3-17). It can be seen from the table that quite a few of the time-series tests did not produce data that supported estimation of biodegradation rate. Nonetheless, comparison of computed degradation rates among products is reflective of the original 40-day BOD time-series data for freshwater and marine conditions where EG-based products exhibited the lowest rates of biodegradation, while the potassium acetate product had the highest rate with PG-based products between the two.

The resulting rate estimates provide a basis for general comparison among formulations. Biodegradation rates observed in the laboratory serve as a tool to compare formulations under controlled, laboratory conditions. They may not be directly applicable to the natural environment because conditions such as mixing, aeration rate, light exposure, and microbial populations vary dependent on site location.

TABLE 3-17 First-Order Decay Rate Constants Computed from 40-Day Biochemical Oxygen Demand Testing with Aircraft and Pavement Deicing and Anti-icing Formulations

		Deicer Product						
		Ethylene Glycol		Propylene Glycol				
		Type I	Type IV	Type I	Type IV	Potassium Acetate Deicer	Sodium Acetate Deicer	Sodium Formate Deicer
Freshwater 20°C	Relative Decay Rate (1/day) (95% confidence interval)	0.091 (± 0.025)	0.086 (± 0.024)	0.238 (± 0.03)	0.251 (± 0.04)	0.407 (± 0.034)	**	**
Marine 20°C	Relative Decay Rate (1/day) (95% confidence interval)	—	—	0.089 (± 0.032)	0.078 (± 0.029)	0.214 (± 0.074)	—	—
Freshwater 5°C	Relative Decay Rate (1/day) (95% confidence interval)	**	**	**	**	0.104 (± 0.019)	0.222 (± 0.04)	**

** Could not determine decay rate.
— Not tested.

SECTION 4

CONCLUSIONS

Literature and Data Review

Literature compiled on the subject of aircraft and airfield deicers and anti-icers provides a valuable base of information to both the research team and the aviation industry as a whole.

The FAA and SAE requirements, guidance, and standards for aircraft and airfield deicers and anti-icers and practices provide limited guidance on environmental characteristics. The only such numerical guidance is provided through SAE, and even then for only the toxicity of Type I ADF products. No guidance is provided for BOD content.

Twenty-five FPDs, 21 surfactants, 11 corrosion inhibitors, 13 thickening agents, six defoamers, nine pH modifiers, five dyes, four oils, and four antioxidants and antimicrobial agents have been identified in literature as potential deicer components. Toxicity data are available for less than one third of these chemicals, and the available data are not always useful or relevant to deicing situations. Further testing will be needed to define the toxicity of individual candidate deicer components.

Most of the research on fate and transport of deicers has focused on the FPDs and, to a lesser extent, on benzotriazole-derived corrosion inhibitors and APE surfactants. Benzotriazoles and APEs have been studied at a small number of airports, but the bulk of research on APEs has been in wastewater treatment and in the context of discharge to receiving waters without treatment. Benzotriazoles have proven to degrade slowly or not at all in the environment. Of concern is the fact that some APE degradation products are more toxic than their parent compounds, express endocrine disruption potential, and have the potential for sorption to sediment particles and persistence in benthic sediments. Although conclusions from the current literature indicate that additional research is necessary to better understand toxicity in ADF and AAF formulations and deicer runoff, available data indicate that the most likely sources of toxicity in PDM are the FPDs.

The primary impact of FPDs on biological treatment systems is increased organic load. The impact of additives on treatment systems is less well understood. NPE can be degraded through biological treatment, but reported details on degradation and byproduct generation are variable. Benzotriazoles are unlikely to be completely biodegraded in biological treatment systems, although they are reported to undergo complete mineralization under ozonation.

The primary source of reported potential impacts on operations and infrastructure from pavement deicers appears to be the potassium ion; sodium-based deicers appear to contribute to a lesser degree. Many of the reported impacts have been traced to other factors, such as poor maintenance or construction practices, and thus addressed through improved maintenance. Catalytic oxidation of carbon-carbon brake components is the most prominent current issue surrounding pavement deicer impacts on aircraft components.

Efforts have been made lately to improve the environmental characteristics of deicers. Toxicities of some Type I ADF formulations have improved in recent years, and some European communities have developed restrictions on deicer components forcing a removal of additives such as triazoles and APE. North American deicer manufacturers indicate that they have eliminated, or are moving towards removal of APE and triazoles from deicer formulations. The BOD of PDM formulations has improved with the introduction of acetate- and formate-based products, although characterization of the toxicity of these PDM products is an area of ongoing study.

Laboratory analysis of deicer runoff samples requires special considerations. BOD determination poses unique challenges that include determination of appropriate dilutions and development of properly acclimated BOD seeds. Standard techniques are not in place for determining deicer additives such as benzotriazoles and APEs. These techniques are currently in flux, necessitating regular review of literature to evaluate the most current methods. Low DO resulting from high BOD complicates toxicity tests involving deicer runoff samples, although strategies have been developed to minimize this issue.

The available literature suggests that acute deicer toxicity at low temperatures is not dramatically different from test results using standard temperatures.

Airfield and Aircraft Components Assessment

Toxicity

Baseline acute toxicity tests on Type I ADF indicated two groupings: one group of Type I products with LC_{50}s averaging about 10,000 mg/L, and a second group with LC_{50}s near 30,000 mg/L. Baseline chronic toxicity of Type I ADF resulted in IC_{25}s less than 4000 mg/L in at least two of the three tested organisms for four out of the five formulations tested.

Type IV AAF products consistently demonstrated much greater toxicity than the Type I products, with LC_{50}s near 2,500 mg/L and lower and IC_{25}s of 1,350 mg/L and lower. PDM toxicity levels are between those of Type I and Type IV formulations. Toxicity results with marine species were similar to those with freshwater test species.

Toxicity in fractionated Type IV and Type I deicer products was associated primarily with APE surfactants and aliphatic alcohol ethoxylate surfactants, with secondary contributions from benzotriazole-derived corrosion inhibitors. Toxicity in pavement deicers is associated primarily with the FPDs.

Oxygen Demand

On a mass basis (i.e., milligrams per kilogram), PG-based ADF and AAF exhibit about 1.85 and 1.6 times greater BOD_5, respectively, than comparable EG-based products. Sodium formate PDM had significantly lower COD than the acetate-based PDMs. BOD and COD results for PDM were consistently lower than those in ADF and AAF. Evaluation of BOD results for the sodium formate PDM was confounded by inhibition of microorganisms presumably due to an additive component.

There appears to be no significant difference between BOD measured in fresh water and BOD measured in marine water tests conducted at 20°C. Tests conducted at low temperatures consistently resulted in lower BOD exertion than standard-temperature tests. The degree of difference between standard- and low-temperature BOD results varied among tested products. Low-temperature marine tests resulted in less degradation than did standard-temperature tests.

SECTION 5
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