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Oxygen Demand of Aircraft and Airfield Pavement Deicers and Alternative Freezing Point Depressants

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Abstract Aircraft and pavement deicing formulations and other potential freezing point depressants were tested for biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Propylene glycol-based aircraft deicers exhibited greater BOD_5 than ethylene glycol-based aircraft deicers, and ethylene glycol-based products had lower degradation rates than propylene glycol-based products. Sodium formate pavement deicers had lower COD than acetate-based pavement deicers. The BOD and COD results for acetate-based pavement deicers (PDMs) were consistently lower than those for aircraft deicers, but degradation rates were greater in the acetate-based PDM than in aircraft deicers. In a 40-day testing of aircraft and pavement deicers, BOD results at 20°C (standard) were consistently greater than the results from 5°C (low) tests. The degree of difference between standard and low temperature BOD results varied among tested products. Freshwater BOD test results were not substantially different from marine water tests at 20°C, but glycols degraded slower in marine water than in fresh water for low temperature tests. Acetate-based products had greater percentage degradation than glycols at both temperatures. An additive component of the sodium formate pavement deicer exhibited toxicity to the microorganisms, so BOD testing did not work properly for this formulation. BOD testing of alternative freezing point depressants worked well for some, there was little response for some, and for others there was a lag in response while microorganisms acclimated to the freezing point depressant as a food source. Where the traditional BOD_5 test performed adequately, values ranged from 251 to 1,580 g/kg. Where the modified test performed adequately, values of BOD_{28} ranged from 242 to 1,540 g/kg.

Keywords Biochemical oxygen demand · Aircraft deicers · Pavement deicers · Freezing point depressant

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1 Introduction

Ensuring the safety of winter flight operations requires removing ice and snow from aircraft surfaces,

preventing ice and snow from accumulating on aircraft surfaces before takeoff, and maintaining ice- and snow-free taxiways and runways. Central to these efforts is the application of aircraft deicing and anti-icing fluids and pavement deicing and anti-icing materials (PDMs) to remove frozen precipitation (deice) and inhibit its subsequent re-accumulation (anti-ice). These products are strictly regulated and must meet Aerospace Material Specification standards for freezing point depression, surface tension, viscosity, materials compatibility, and other performance characteristics. Freezing-point depressants (FPDs) in aircraft deicing and anti-icing fluids are typically propylene glycol, ethylene glycol, or rarely, diethylene glycol. Aircraft deicing and anti-icing fluids also contain water and additives which include corrosion inhibitors, surfactants, thickeners, dyes, flame retardants, defoamers, and pH buffers (U.S. Environmental Protection Agency 2000). The primary FPDs in PDMs are potassium and sodium salts of acetate and formate, urea, and, to a lesser degree, propylene glycol, and ethylene glycol.

Aircraft and pavement deicing activities are conducted outdoors, over large areas of the airport, and typically under conditions of wintertime precipitation. As a result, some portions of the applied deicing products are subject to mixing with runoff and discharge to the environment via the airport's stormwater system. Environmental concerns associated with these discharges relate to the nature of the materials in the deicing products. A primary concern that has been recognized since at least the 1970s is the biochemical oxygen demand (BOD) associated with readily biodegradable FPDs in these products (Schulz and Comerton 1974).

At many airports, a portion of the aircraft and pavement deicers are collected and treated with biological treatment systems, and the remainder is released into the environment (U.S. Environmental Protection Agency 2000). Two of the key characteristics of aircraft and airfield deicing discharges are cold temperatures and untreated biodegradable materials as the primary source of BOD. These are relatively unique to this situation and require special consideration. Research on low temperature biodegradation of deicers has been conducted to determine potential for onsite degradation in the airport environment. A study of deicer degradation with seed microorganisms from airport impervious surfaces indicated decreasing decay rates with decreasing temperatures (Revitt and Worrall 2003). A mixture of untreated potassium acetate, propylene glycol, and ethylene/diethylene deicer formulations degraded by 32.9%, 30.2%, and 21.4%, respectively at 8°C, 4°C, and 1°C in a 5-day test period. Another study of degradation in soils also demonstrated the lowest decay rates at −2°C and the highest at 25°C (Klecka et al. 1993). Other research showed very little propylene glycol degradation in top soil at 4°C and that degradation of deicers occurred in the topsoil with greatly reduced degradation as the fluid migrated through the subsoil leading to the conclusion that these deicers have the potential to percolate into deeper soil horizons or groundwater (Jaesche et al. 2006).

The potential for aircraft and airfield deicing runoff to contribute to decreased dissolved oxygen (D.O.) in receiving waters is a function of the amount of biodegradable deicing materials in stormwater discharges, the rate at which biodegradation occurs, and the ability of the receiving waters to replenish D.O. 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 oxygen depletion in receiving water may actually be less. Thus, accurately characterizing the BOD content of deicers and how the resulting oxygen demand is exerted under ambient conditions is central to understanding the implications of discharges at any given facility.

This paper represents a portion of the initial research to develop alternative deicer formulations with reduced environmental impact compared to current-use formulations (Airport Cooperative Research Program 2009, 2010). Two primary topics are covered: (1) characterization of the BOD and chemical oxygen demand (COD) of current-use aircraft and airfield pavement deicing products and (2) BOD and COD measurements of FPDs that had been identified as potentially viable alternatives to the FPDs in current-use products. Important aspects of the research included measuring BOD at low temperatures representative of ambient winter time conditions and in marine water and identification of complications in the procedures for measuring BOD in a variety of high concentration samples.

2 Methodology

Laboratory analyses were conducted on seven commercial deicer formulations (Table 1) and 24 pure chemicals that had been identified as possible alternative FPDs (Table 2). The commercial formulations consisted of four aircraft and three pavement deicer products representative of the categories of deicers commonly used.

A mix of traditional and modified BOD analyses were conducted on these samples (Table 3). It should be noted that not all analyses were conducted on all samples. For example, only a subset of commercial deicer products and no candidate FPDs were subjected to BOD analysis using marine dilution water. Details of the analyses are presented below.

2.1 Traditional Analyses

COD analyses were performed according to American Society of Testing and Materials method D1252-88(B) (American Society for Testing and Materials International 1993). Briefly, the COD test uses hexavalent chromium (Cr^{+6}), a strong inorganic oxidant, to assess the potential oxygen demand of an organic waste. The reduction of Cr^{+6} to Cr^{+3} is directly proportional to the COD value. Traditional 5-day BOD (BOD_5) analyses were performed using standard 300 mL bottles according to *Standard Methods for the Examination of Water and Wastewater*, method 5210B (American Public Health Association, American Water Works Association, and Water Environment Federation 1995). The dilutions for BOD_5 were preliminarily determined based on judgments made by experienced analysts and informed by COD results. In some cases, repeated testing was needed to fine-tune dilutions.

2.2 Modified BOD Method

The conventional BOD analysis involved preparing serial dilutions of the test material in standard 300 mL BOD bottles and adding laboratory pure water fortified with nutrients, saturated with D.O., and inoculated with microorganisms. The D.O. concentration was measured shortly after preparation and the BOD bottles incubated in the dark at 20°C for 5 days. At the end of the 5-day test period, the D.O. concentration was measured again. The change in D.O. concentration was used to compute the BOD_5. Samples with a very high oxygen demand present a special challenge in the analysis because D.O. reaches saturation in the bottle at roughly 9.0 mg/L depending on the elevation and atmospheric pressure. Consequently, massive dilutions are required to ensure that D.O. limitations do not occur during the test period. To address this issue, a modification of Method 5210B was developed using large volume bottles and periodic reaeration of the samples. This method was used to characterize biodegradability of the deicer formulations in terms of oxygen demand exerted over time at 20°C and 5°C in fresh water and artificial marine water.

The modified method involved time-series BOD analyses using 2,120-mL custom BOD bottles. Ultimate BOD was estimated based on the ratio of COD and BOD_5 to get measurable demand without depleting all oxygen in the sample bottle. This relation was then used to prepare dilutions based on weight per volume. Because the relation between COD and BOD_5 varied by product, there were no strict guidelines for this, but analyst experience and judgment was used to determine final dilutions. Final dilutions ranged from 0.02 to 0.12 g of product for the 2,120-mL bottles. Marine water samples were prepared

Table 1 List of commercial deicer formulations analyzed

Deicer product	Freezing point depressant content (%)	Specific gravity
Ethylene glycol-based type I aircraft deicing formulation	92	1.1
Ethylene glycol-based type IV aircraft anti-icing formulation	64	1.1
Propylene glycol-based type I aircraft deicing formulation	88	1.04
Propylene glycol-based type IV aircraft anti-icing formulation	50	1.06
Potassium acetate-based liquid pavement deicing formulation	50	1.28
Sodium acetate-based solid pavement deicing formulation	96	n/a
Sodium formate-based solid pavement deicing formulation	98	n/a

Table 2 List of candidate freezing point depressants analyzed

Candidate FPD	Chemical Abstracts Service (CAS) number	Potential application (A, aircraft; P, pavement)
1,1,1-Trimethanolethane	77-85-0	P
1,2-Propylene glycol	57-55-6	A, P
1,3-Butanediol	107-88-0	A, P
1,3-Propylene glycol	504-63-2	A, P
2-(2-Ethoxyethoxy)-ethanol	111-90-0	A, P
2-(2-Methoxyethoxy)-ethanol	111-77-3	A, P
2,2-Dimethyl-1,3-dioxolane-4-methanol	100-79-8	A, P
2,3-Butanediol	513-85-9	A
2-Methyl-1,3-propanediol	2163-42-0	A, P
4-Methyl-γ-butyrolactone	108-29-2	A
Calcium propionate	4075-81-4	P
D-Gluconic acid δ-lactone	90-80-2	P
Diethylene glycol	111-46-6	A, P
Dipropylene glycol	25265-71-8	A, P
Disodium succinate	150-90-3	P
Ethylene carbonate	96-49-1	A, P
Glycerol	56-81-5	A, P
L-Tartaric acid dipotassium salt	921-53-9	P
Propylene carbonate	108-32-7	A
Sodium acetate	127-09-3	P
Triethylene glycol	112-27-6	A, P
Trimethylolpropane	77-99-6	P
Tripotassium citrate	6100-05-6	P
Xylitol	87-99-0	P

under the general guidelines of the International Standards Organization method 16221. The D.O. in the sample bottles was monitored at 5, 15, and 28 days for all samples with an additional measurement at 40 days for the deicer products. As D.O. concentrations approached 2.0 mg/L, a level that would potentially inhibit biological activity, the samples were reaerated using filtered compressed air, the D.O. concentration was measured, and the samples returned to the incubator. The modified BOD analyses were conducted in quintuplicate for current-use deicer samples and quadruplicate for candidate FPD samples.

Freshwater inoculums were prepared using primary wastewater (Madison Wisconsin Metropolitan Sewerage District, Madison, WI, USA). A marine water BOD seed inoculum was prepared from a suspension of estuarine sediment collected near Kiawah Island, South Carolina, and artificial marine water.

Attempts were made to acclimate the freshwater and marine seed inoculums to mixtures of deicer products to better approximate receiving water conditions as described previously (Airport Cooperative Research Program 2009). This approach did not work well most likely due to toxicity effects of deicer additives to microorganisms when deicers are present at high concentrations (Cornell et al. 2000). Instead, un-acclimated inoculums were used for the 40-day studies. The implications of this observation are primarily the reduction of initial degradation rates as discussed in Section 4.4 below.

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 on aliquots from the 40-day 20°C and 5°C BOD samples confirmed that adequate microbial populations (at least 10^5 organisms per mL) were present throughout the exposure period to conduct the test.

Table 3 Laboratory analyses conducted on commercial deicer formulations and candidate freezing point depressants

Parameter	Temperature (°C)	Dilution water (s)	Samples analyzed	Bottle size	Replicates
COD	20	n/a	P, F	n/a	3
BOD_5 conventional	20	Fresh	P, F	300 mL	3
BOD_5	20	Fresh	P, F		
BOD_{15}		Marine	P	2,120 mL	5
BOD_{28}	5	Fresh	P		
BOD_{40} modified		Marine	P		

P Commercial deicer and anti-icer formulations, *F* candidate freezing point depressants

2.3 Quality Control

Quality control samples consisted of blanks, control standards, and replicates. For BOD, laboratory blanks were tested along with the samples to correct for the contribution of seed material, demand exerted by the dilution water, and potential BOD contribution from repeated D.O. measurements during the test period. Five replicate glucose–glutamic acid controls were also tested in fresh water at 20°C and 5°C. Results were used to assess precision and method bias.

Controls, matrix spikes using potassium hydrogen phthalate, and blanks were performed as specified by the reference method (American Public Health Association, American Water Works Association, and Water Environment Federation 1995). Standard Methods 21st Edition Method 5210 C Ultimate BOD Test states that the ultimate BOD for glucose–glutamic acid (GGA) control samples is between 308 and 321 mg/L, depending on the extent of nitrification (American Public Health Association, American Water Works Association, and Water Environment Federation 1995, 2005). Results for GGA samples using the modified method indicate a typical decay pattern over the test period with the 40-day 20°C BOD approximately 8–12% higher than the reference range of values (Table 4). This is an acceptable performance for a biologically driven test. As might be expected with reduced degradation rates at low temperatures, the 40-day 5°C BOD using the modified method was significantly lower than the reference range.

Controls for COD, matrix spikes using potassium hydrogen phthalate, and blanks were performed as specified by the reference method. Recoveries ranged from 78% to 116% (mean=97.3%, SD=6.4%, n=9) and all blanks were at or below the limit of detection of 8.5 mg/L.

Replicate analyses for COD, traditional BOD_5, and modified BOD testing were done for each of the products and FPDs studied. Replicate COD analyses resulted in a relative standard deviation from 0.4% to 5.5% for all tests (n=3 or 4). Replicates for traditional BOD_5 analysis resulted in a relative standard deviation of 0.5–7.7% (n=3) for deicer products and less than 10% relative standard deviation (n=4) for all except four of the FPDs (14% for 2,2-dimethyl-1,3-

Table 4 BOD of five glucose–glutamic acid control samples using the modified method at 20°C and 5°C with measurements at 5, 15, 28, and 40 days

Day	BOD (mg/L) at 20°C					BOD (mg/L) at 5°C				
	Mean	Standard deviation	% RSD	95% C.I.	Difference from BOD_{ult} (%)	Mean	Standard deviation	% RSD	95% C.I.	Difference from BOD_{ult} (%)
5	205	2.7	1.3	3.3	−36.1	117	4	3.4	4.9	−63.6
15	310	17.5	5.66	21.8	−3.4	189	3.2	1.68	3.9	−41.1
28	333	12.8	3.84	15.9	3.7	220	5.7	2.59	7.1	−31.5
40	346	4.3	1.25	5.4	7.8	228	6.1	2.66	7.5	−29.0

BOD_{ult} ultimate BOD = 321 mg/L, Standard Methods of the Examination of Water and Wastewater, method 5210C, American Public Health Association, American Water Works Association, and Water Environment Federation (2005)

dioxolane-4-methanol, 16.8% for disodium succinate, 30% for propylene carbonate, and 11% for xylitol).

Final replicate results at day 40 using modified BOD methods for deicer product testing (n=5) resulted in relative standard deviations between 1.0% and 7.2% for freshwater at 20°C, 3–14% for marine water at 20°C, and 2.8–9.4% for freshwater at 5°C except for the sodium formate deicer which had a relative standard deviation of 29%. The marine water tests at 5°C did not result in sufficient D.O. depletion to achieve valid test results for the propylene glycol products. The relative standard deviation for the potassium acetate deicer product was 13.1% at day 40.

Final replicate results at day 28 using modified BOD methods for FPD testing resulted in a relative standard deviation of 10% or less (n=3) for all samples except 2-methyl-1,3-propanediol (12%), diethylene glycol (45%), dipropylene glycol (52%), and trimethylolpropane (32%).

3 Results

The results of the laboratory analyses are presented separately for the commercial deicer formulations and the candidate FPDs.

3.1 Commercial Deicer Formulations

There was wide variability in COD and BOD_5 results for the commercial deicer formulations (Table 5). This variability is the result of differences in the BOD of the constituent FPDs and the concentration of the FPDs in each product. For the aircraft deicers and anti-icers, propylene glycol and ethylene glycol are the primary sources of oxygen demand, while acetate and formate are the primary sources in the PDMs. To normalize the results for the concentrations of these FPDs in the tested products, COD and BOD_5 were calculated "as primary source" (i.e., as propylene glycol, as ethylene glycol, as acetate, or as formate). Presenting the data in this form allows for direct comparison of the same FPD in different formulations. Results from the two ethylene glycol formulations are similar, as are results from the two propylene glycol formulations and results from the two acetate-based formulations.

The sodium formate-based product was the only formulation that exhibited an apparent inhibitory effect on microorganisms during BOD_5 testing. The evidence of inhibition was an observed decrease in measured BOD with increasing sample concentration (Fig. S1, supporting information). This phenomenon is often referred to as a "sliding" BOD. As sample concentration increases, so does the constituent that

Table 5 COD and traditional BOD_5 for selected aircraft and airfield deicer and anti-icer formulations

Formulation	COD		BOD_5		Values expressed as primary source of oxygen demand[a, b]		
	mg/kg	mg/L[c]	mg/kg	mg/L[c]	Primary source	COD (mg/L)	BOD_5 (mg/L)
EG type I	1,180,000	1,050,000	492,000	439,000	Ethylene glycol	1,280,000	535,000
EG type IV	826,000	772,000	331,000	309,000	Ethylene glycol	1,290,000	517,000
PG type I	1,420,000	1,380,000	990,000	961,000	Propylene glycol	1,610,000	1,130,000
PG type IV	842,000	818,000	539,000	523,000	Propylene glycol	1,680,000	1,080,000
Potassium acetate (liquid)	315,000	250,000	247,000	196,000	Acetate	1,050,000	821,000
Sodium acetate (solid)	700,000	NA	571,000	NA	Acetate	1,010,000	826,000
Sodium formate (solid)	242,000	NA	–[d]	NA	Formate	373,000	–[d]

[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

[b] Oxygen demand as primary source; oxygen demand of product / (fraction of FPD in product × molar fraction of primary source in FPD compound)

[c] Results in milligram per liter are computed by dividing results expressed in milligram per kilogram by formulation specific gravity from Table 1

[d] BOD results were not reliable for sodium formate

inhibits the microbial activity (Stover and McCartney 1984). Microtox tests were conducted on the sodium formate formulation and sodium formate FPD to assess toxicity to microorganisms (Airport Cooperative Research Program 2009). The results show the formulated product exhibiting greater toxicity than the pure FPD. The 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 in the laboratory tests.

Results also suggest significant differences in rates of biodegradability among the FPDs, as reflected in the fraction of COD (an estimate of BOD_{ult}) exerted at 5 days (Table 5). For example, about 41% of the BOD_{ult} in the ethylene glycol-based deicers was exerted at 5 days, while 65–70% of the BOD_{ult} in the propylene glycol-based deicers was exerted over the same period.

Table 6 presents the results of the time series using the modified BOD method in terms of the primary source of BOD in each formulation. The sodium

Table 6 BOD of deicers and anti-icers using the modified method at 20°C and 5°C with measurements at 5, 15, 28, and 40 days

Formulation	Day	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	–[a]	ND[b]	–[a]
	15	871,000	–[a]	ND[b]	–[a]
	28	904,000	–[a]	200,000	–[a]
	40	1,000,000	–[a]	702,000	–[a]
EG type IV (as ethylene glycol)	5	306,000	–[a]	ND[b]	–[a]
	15	891,000	–[a]	ND[b]	–[a]
	28	966,000	–[a]	ND[b]	–[a]
	40	1,070,000	–[a]	297,000	–[a]
PG type I (as propylene glycol)	5	957,000	391,000	ND[b]	ND[b]
	15	1,270,000	1,300,000	340,000	ND[b]
	28	1,320,000	1,410,000	950,000	ND[b]
	40	1,430,000	1,460,000	986,000	<208,000[b]
PG type IV (as propylene glycol)	5	984,000	296,000	ND[b]	ND[b]
	15	1,280,000	1,250,000	ND[b]	ND[b]
	28	1,320,000	1,410,000	988,000	ND[b]
	40	1,430,000	1,450,000	1,220,000	<562,000[b]
Potassium acetate deicer (as acetate)	5	864,000	748,000	320,000	ND[b]
	15	1,020,000	944,000	807,000	ND[b]
	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[b]	–[a]	631,000	–[a]
	15	1,060,000	–[a]	797,000	–[a]
	28	981,000	–[a]	916,000	–[a]
	40	1,010,000	–[a]	948,000	–[a]
Sodium formate deicer[b] (as formate)			ND[b, c]		

Results presented as concentration of primary source of oxygen demand

[a] Analyses not included in this study

[b] Did not meet oxygen depletion criteria for reporting

[c] 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

formate solid runway deicer again exhibited an inhibitory effect, and the results are considered unreliable.

3.2 Candidate Freezing Point Depressants

The BOD_5, BOD_{15}, BOD_{28}, and COD results for 24 candidate FPDs are summarized in Table 7 listed in order of increasing COD. There were problems encountered with the BOD tests for some FPDs that limited the utility of data. Adequate results could not be obtained for nine of the candidate FPDs for the traditional BOD_5 test and six of the FPDs for the 28-day test. Another six FPDs exhibited significant lags in BOD exertion indicating that the microorganisms needed time to adapt to the food source. Theoretical ultimate oxygen demand was computed and published elsewhere (Airport Cooperative Research Program 2010). The ratio of theoretical oxygen demand to COD varied between 0.74 and 1.23 with 80% of values between 0.84 and 1.08.

4 Discussion

A number of noteworthy issues came out of the results of this research. These include differences in rates of

Table 7 COD and BOD of candidate FPDs using the modified method at 20°C with measurements at 5, 15, and 28 days

FPD	ThOD[a] (g/kg)	COD (g/kg)	BOD_5 (g/kg)	BOD time-series (g/kg)		
				5 days	15 days	28 days
L-Tartaric acid dipotassium salt	432	341	231	213	239	242
Tripotassium citrate	345	449	309	262	297	301
Disodium succinate	592	684	481	466	533	533
Sodium acetate	683	747	552	586	653	667
2-(2-Methoxyethoxy)-ethanol	1,730	883	–[b]	24	517	641
Ethylene carbonate	908	899	34[c]	5.9	57.6	96.9[c]
D-Gluconic acid δ-lactone	988	976	660	–[b]	–[b]	–[b]
Calcium propionate	1,120	1,090	823	791	913	936
Xylitol	1,160	1,170	585	644	915	979
Glycerol	1,220	1,190	810	846	985	1,000
Propylene carbonate	1,250	1,200	33.5[c]	–[b]	–[b]	–[b]
Diethylene glycol	1,510	1,500	ND[c]	18.5	128	618
Triethylene glycol	1,600	1,610	ND	53.6	398	560
1,2-Propylene glycol	1,680	1,620	973	1,020	1,270	1,310
1,3-Propylene glycol	1,680	1,640	731	814	1,070	1,190
1,1,1-Trimethanolethane	1,730	1,680	<1,200[d]	6.3	8.1	406
2,2-Dimethyl-1,3-dioxolane-4-methanol	1,820	1,780	10.8[c]	–[b]	–[b]	–[b]
Trimethylolpropane	1,910	1,810	<1,200[d]	−17	−21	660
2,3-Butanediol	1,950	1,820	1,200	–[b]	–[b]	–[b]
1,3-Butanediol	1,950	1,830	820	843	1,390	1,450
2-Methyl-1,3-propanediol	1,950	1,850	ND	807	1,450	1,480
Dipropylene glycol	1,910	1,860	1,580	12	81	935
2-(2-Ethoxyethoxy)-ethanol	1,910	1,880	1,100	399	1,490	1,540
4-Methyl-γ-butyrolactone	1,920	1,880	814	–[b]	–[b]	–[b]

[a] Theoretical oxygen demand is computed as ThOD = 32×number of carbon atoms+8×number of hydrogen atoms+16×number of oxygen atoms

[b] Not determined

[c] BOD could not be determined or value is unacceptably low due to suspected inability to find optimum sample to organism ratio

[d] No measurable demand from BOD_5 analysis

biodegradation of the formulations and candidate FPDs, inhibition of microorganisms by the tested formulations, and efficacy of the seed inoculums for different sources of BOD. These are discussed in the following subsections.

4.1 Biodegradability of Deicer Products

The biodegradability of deicers and the rate at which the BOD is exerted are important considerations when assessing the impact of BOD discharges on receiving water D.O. For a given BOD_{ult} and a fixed set of discharge conditions, a slower rate of biodegradation will have a reduced impact on receiving water D.O. because the balance between the rates of D.O. consumption (i.e., BOD exertion) and reaeration processes that replenish D.O. will be more advantageous to maintaining adequate D.O. Under certain conditions, a formulation with a higher BOD_{ult} but slower rate of biodegradation could have a lesser impact on receiving water D.O. than a formulation with a lower BOD_{ult} but faster rate of biodegradation.

An indication of the biodegradability of each deicer product may be gained through comparison of COD and BOD_5 results using COD as an estimate of BOD_{ult} (American Public Health Association, American Water Works Association, and Water Environment Federation 1995). Relative comparisons can be made of how fast BOD is exerted among deicer products by looking at percent degradation ([BOD / COD]×100). Biodegradability computed this way for traditional BOD_5 indicates the greatest biodegradation observed from acetates (79–82%), the next greatest with the propylene glycol-based aircraft deicers (64-70%), and the least with the ethylene glycol-based products (40–42%). Biodegradation in the 20°C tests at 40 days ranged from 78% to essentially 100% for the freshwater and the marine water tests (Fig. 1a, c). Values greater than 100% reflect measurement error inherent in the analytical methods. As before, the acetate-based deicers displayed the fastest biodegradation, followed in decreasing magnitude by the propylene glycol-based aircraft deicers, and the ethylene glycol-based products. The only notable difference between freshwater and marine water results was that the marine

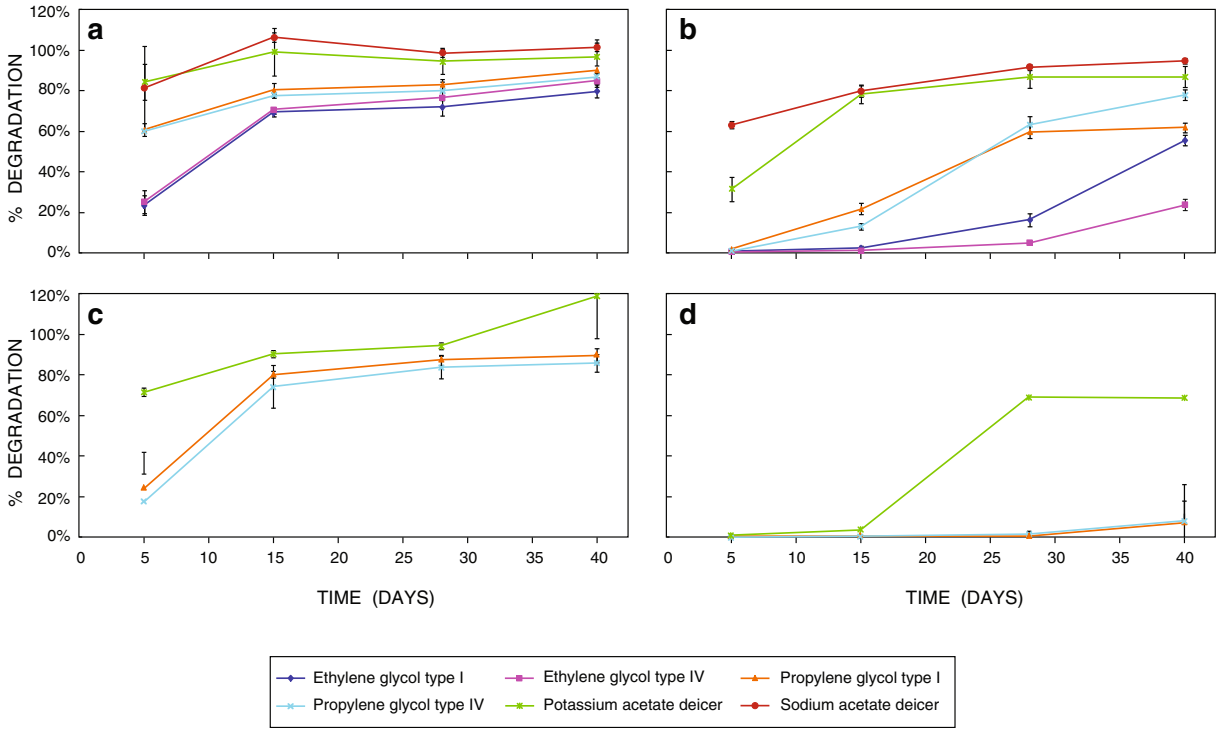

Fig. 1 Percent biodegradation of selected aircraft and airfield deicers and anti-icers based on a 40-day BOD time series using the modified method at **a** 20°C in freshwater, **b** 5°C in freshwater, **c** 20°C in marine water, and **d** 5°C in marine water. *Error bars* represent 95% confidence intervals

water tests exerted less oxygen demand through the fifth day than that in freshwater tests. Results beyond 5 days were similar.

Results of the modified method freshwater tests at 5°C (Fig. 1b) indicate 23–55% degradation for ethylene glycol products, 61–77% degradation for propylene glycol products, 86% for the potassium acetate product, and 94% for the sodium acetate product. Again, the acetates generally degraded fastest, whereas the rates of degradation of the propylene glycol-based fluids were slower, and those of the ethylene glycol-based products were slower still.

In the marine water tests at 5°C, propylene glycol formulations degraded less than 10% during the test period, whereas the potassium acetate liquid PDM degraded by 69% (Fig. 1d). The potassium acetate results show a pronounced lag period in the first 15 days, followed by a large increase in degradation by day 28.

Comparison of 5°C test results with the 20°C test results in both freshwater and marine water indicates 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. An estuarine sediment suspension was used as the seed inoculum for the marine studies. The organisms were likely facultative in nature and adapted to the low oxygen concentrations typical in sediment and required time to adapt to the higher oxygen levels in the studies. The lag was more pronounced in 5°C studies because of the lower temperature resulting in reduced microbial activity and slower adaptation.

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. Field conditions such as mixing, aeration, temperature, vegetation, lighting, and the exact community of microorganisms cannot be duplicated in the laboratory. Consequently, precise extrapolation of the lab results to in situ reductions cannot be estimated with available data. For instance, established microorganism biofilms attached to the streambed downstream from airports have been observed in abundance (Koryak et al. 1998; Corsi et al. 2001). These attached microorganisms are absent in laboratory tests, but have the potential to contribute to BOD exertion in receiving streams.

Finally, relative BOD decay rates were estimated with a nonlinear regression technique following a first-order decay model (Streeter and Phelps 1925):

First-Order Decay Model

$$BOD_t = BOD_{ult} \times \left(1 - e^{-kt}\right)$$

Where:

BOD_t	BOD exerted at time t (mg/L)
BOD_{ult}	Ultimate BOD (mg/L)
K	First-order decay rate (day^{-1})

Decay rates were estimated for those formulations that had acceptable BOD measurements from day 5 to day 40 (Table 8). Formulations that exhibited significant lag periods did not fit the first-order model. Consequently, decay rates were not determined for these products. Ten of the 17 time-series test combinations produced data suitable for estimating biodegradation rate. Comparison of computed degradation rates among products is consistent with the original

Table 8 Estimated first-order decay rate constants computed from time-series modified BOD method results from aircraft and pavement deicing and anti-icing formulations

	Deicer product: relative decay rate (1/day) (95% confidence interval)						
	Ethylene glycol		Propylene glycol		Potassium acetate deicer	Sodium acetate deicer	Sodium formate deicer
	Type I	Type IV	Type I	Type IV			
Freshwater 20°C	0.091 (±0.025)	0.086 (±0.024)	0.238 (±0.03)	0.251 (±0.04)	0.407 (±0.034)	–[a]	–[a]
Marine water 20°C	–[b]	–[b]	0.089 (±0.032)	0.078 (±0.029)	0.214 (±0.074)	–[b]	–[b]
Freshwater 5°C	–[a]	–[a]	–[a]	–[a]	0.104 (±0.019)	0.222 (±0.04)	[a]

[a] Could not determine decay rate

[b] Not tested

40-day BOD time-series data for freshwater and marine conditions; ethylene glycol-based products exhibited the lowest rates of biodegradation, followed by propylene glycol-based products. The potassium acetate product had the highest biodegradation rate.

BOD values determined through the course of this research compare well to those from previous studies. In a review of previous testing, the U.S. Environmental Protection Agency (2000) reported that values for BOD_5 for ethylene glycol ranged from 400,000 to 700,000 mg/kg, the value reported for propylene glycol was 1,000,000 mg/kg, the range for potassium acetate was 140,000 to 300,000 mg/kg, the value for sodium acetate was 580,000 mg/kg, and the value for sodium formate was 230,000 mg/kg.

It should be recognized that 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 depending on site location. For example, a field study to examine biodegradation of type I deicer over a 5-km reach of receiving stream resulted in a first-order decay rate of 0.80 day with water temperatures ranging from 6.5°C early during the day of the study to 20.0°C later in the day (Corsi et al. 2001). This stream had an abundant population of attached biomass in the stream and likely had acclimated microorganisms suspended in the water column given that the study was conducted in April after 5 months of deicing activity.

4.2 Biodegradability of Freezing Point Depressants

Biodegradability of those FPDs where valid data could be obtained was examined by comparing BOD_5, BOD_{15}, and BOD_{28} with the COD results. BOD_5 biodegradation ranged from 0% for trimethylolpropane to 75.8% for sodium acetate, BOD_{15} ranged from 0% for trimethylolpropane to 87% for sodium acetate, and BOD_{28} biodegradation ranged from 10.8% for ethylene carbonate to 89.3% for sodium acetate (Fig. 2).

First-order decay rates were determined for some FPDs and are presented in Table 9. Decay rates generally conformed to first-order kinetics except for seven FPDs. These compounds did not follow the first-order kinetics primarily because of the long lag period (Table 7).

An explanation for the observed lag periods may be found in the response of microorganisms in the BOD test. The BOD analysis requires five key components: a food (carbon) source, microorganisms adapted to that carbon source, oxygen, the appropriate temperature, and a source of nutrients to provide optimal growth for organisms. If any of these components are missing or inadequate, the test results will be anomalous. Oxygen, temperature, and nutrient levels are operationally controlled in the BOD testing process. However, microorganism and carbon levels are sample dependent and can be especially problematic in the analysis of FPDs. Organisms may not readily adapt to the carbon source in the FPD which may explain the lag observed (example provided in Fig. 3). Microorganism population can also be limiting when there is an inadequate number of organisms at the beginning of the test or if the organisms are slow in adapting to the FPD as a food source. The observed significant lag times in the time-series BOD results could be caused by either, or both, of these conditions.

The BOD testing for 2-methyl-1,3-propanediol and diethylene glycol did not provide acceptable results even after multiple attempts. Twelve dilutions were prepared on the 2-methyl-1,3-propanediol in the final attempt to obtain BOD_5 results. None of the 12 dilutions met the depletion and residual D.O. criteria. The 0.001-mL/L dilution had too little oxygen depletion and the 0.002-mL/L dilution had too much depletion. Under most circumstances, this dilution series would have produced at least two valid BOD_5 results. Similar results were observed for diethylene glycol. The BOD_5 results for dimethyl malonate, 1,1,1-trimethanolethane, and triethylene glycol exhibited a significant lag period, which is a characteristic of the inability of the microorganisms to adapt to the food source.

The problems observed with the disodium succinate and diethylene glycol may be attributed to two factors: (1) an inability of microorganisms to adapt to the FPD as a food source and (2) an inability to find the right carbon, nutrient to organism ratio. It may be possible to adapt the microorganisms to each specific FPD; however, this would require extensive work and it would do little to reflect environmental conditions.

The utility of the estimated laboratory decay rates to predict behavior of FPDs in the environment is limited given the observations in this research. Wastes generally decay at a more rapid rate in the

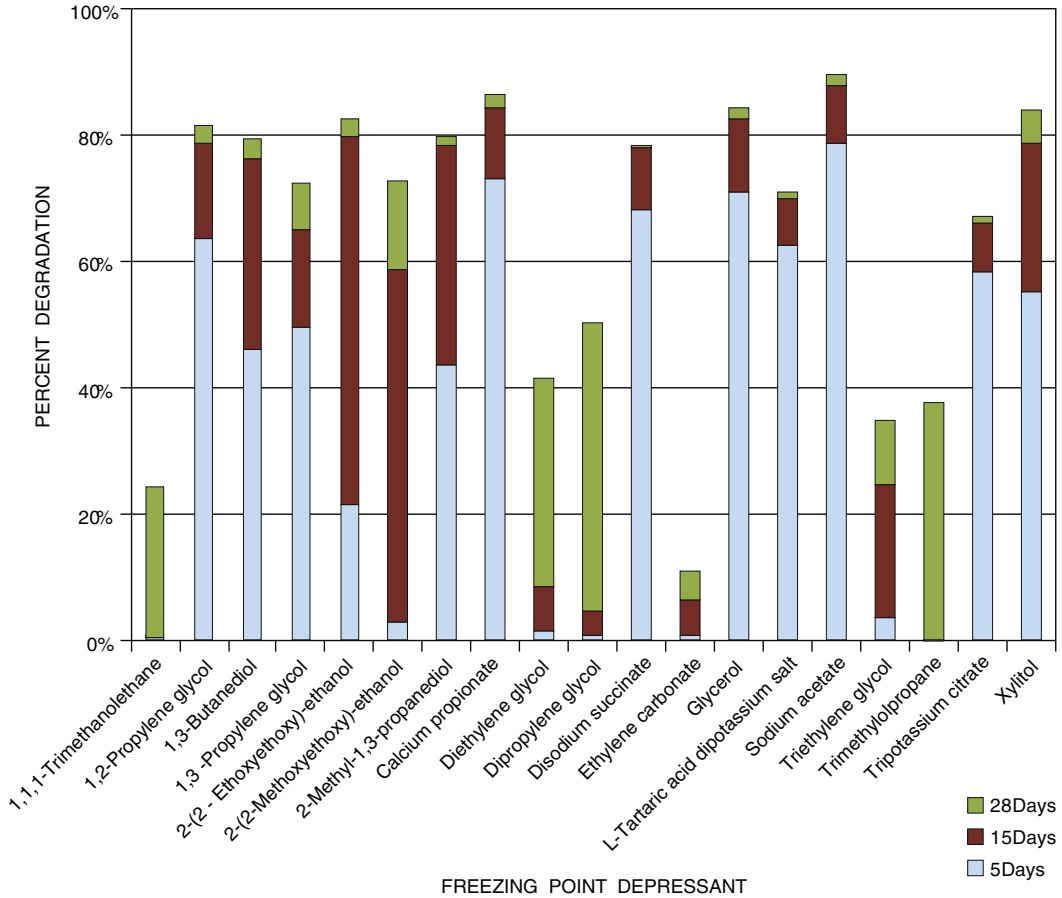

Fig. 2 Percent biodegradation of freezing point depressants from 5-, 15-, and 28-day measurements as compared to chemical oxygen demand

environment than in laboratory tests because they are continually mixed, aerated, exposed to different lighting conditions, and subjected to organisms attached to stream substrates that are adapted to the particular waste (Vaishnav and Korthals 1988). FPDs that decay rapidly in the laboratory will likely decay more rapidly under environmental conditions; however, the measured decay rate of FPDs that biodegrade slowly in the laboratory may not provide good estimate of how they will behave in the environment.

4.3 Inhibitory Effects

The sodium formate formulation exhibited an inhibitory effect on the BOD test microorganisms. The lowest concentration tested was 0.02 g/300 mL, or about 66.7 mg/L, which resulted in the highest observed BOD_5 for the formulation of approximately 12,000 mg/kg (Fig. SI, supporting information). The COD of the formulation was 243,242 mg/kg, which suggests that significant inhibition was occurring at this concentration. The implication of this observation is that BOD analyses of environmental samples containing the sodium formate PDM formulation may not accurately assess the true oxygen demand potential. It is possible, however, that organisms in receiving water may adapt to this product much like those in wastewater treatment plants that adapt to the mix of organic wastes to which they are routinely exposed. Site-specific studies may be required to better understand the potential inhibitory effects and their implications.

Considering previous research results, it is possible that inhibition of microorganisms may need to be considered for other deicers. Biodegradation testing was conducted with and without various additives to evaluate inhibition of microorganisms (Cornell et al.

Table 9 First-order decay rates of candidate FPD based on BOD_{28} studies

FPD	Mean decay rate constant (K)	% RSD decay rate	Decay rate constant of deicer products
2-(2-Ethoxyethoxy)-ethanol	0.117	0.057	–
1,3-Butanediol	0.136	0.024	–
2-Methyl-1,3-propanediol	0.151	0.027	–
1,3-Propylene glycol	0.158	0.162	–
Xylitol	0.179	0.01	–
1,2-Propylene glycol	0.227	0.015	0.25
Glucose–glutamic acid control	0.26	0.126	–
Glycerol	0.354	0.027	–
Calcium propionate	0.364	0.027	–
Tripotassium citrate	0.408	0.057	–
L-Tartaric acid dipotassium salt	0.445	0.016	–
Disodium succinate	0.486	0.164	–
Sodium acetate	0.565	0.043	0.22
Ethylene carbonate	–[a]		–
Diethylene glycol	–[a]		–
1,1,1-Trimethanolethane	–[a]		–
2-(2-Methoxyethoxy)-ethanol	–[a]		–
Trimethylolpropane	–[a]		–
Dipropylene glycol	–[a]		–
Triethylene glycol	–[a]		–

[a] Decay rate could not be determined due to long initial lag period

2000). Biodegradation rates were consistently less when additives were present as compared to pure glycol. Given the large differences in additive composition in different deicer formulations and the results seen in the present research, this type of inhibition is likely to be formulation dependent.

4.4 Seed Inoculum

The anomalous results observed for some of the formulations and FPDs may be partially attributed to the seed inoculums used in the BOD tests. The use of acclimated inoculums is a common practice in BOD

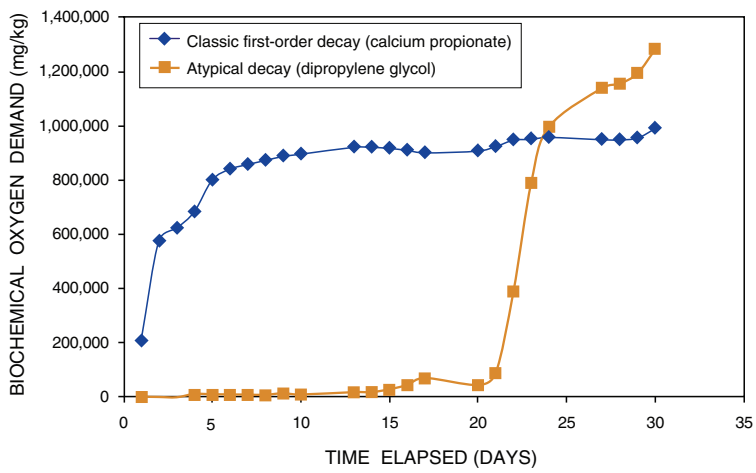

Fig. 3 Comparison of the BOD characteristics from decay of two freezing point depressants at 20°C

testing particularly when the waste type or compound to be studied is known (American Public Health Association, American Water Works Association, and Water Environment Federation 1995). Use of unacclimated seed inoculums will generally not affect the final outcome of long-term tests, but may result in a slightly longer initial lag period while the organism population acclimates to the food source and grows.

When an acclimated inoculum is prepared, a lag phase may 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 organisms in the seed inoculums did not flourish. This may have been caused by a less than ideal carbon-to-organism ratio or the organisms simply did not adapt to the FPD mixture. A more likely cause could be attributed to the carbon sources in the seed FPD feed stock which was prepared from multiple deicer products. The sodium formate PDM product showed inhibitory affects in both the 5- and 40-day BOD tests. This product may have introduced an inhibitory effect on the organisms in the seed inoculums as well. Two attempts were made to prepare the seed inoculums by varying the feeding rate and by adding incremental amounts of estuarine sediment supplemental organisms. However, similar results were observed in both instances. Further seed acclimation trials were discontinued at this point in the research with the understanding that there could be a slightly longer lag in the test period as the organism population adapted to each FPD during the test period. In future research, it is possible that adapted seed inoculums could be developed for each individual FPD.

5 Conclusions

Conclusions for this study can be broken into two major topics: first, the results from aircraft deicer and FPD testing and, second, methodological considerations. Results of BOD testing for current-use aircraft deicers indicated that propylene glycol-based formulations exhibited greater BOD_5 compared to ethylene glycol-based products. In addition, ethylene glycol-based products had lower degradation rates than propylene glycol-based products. Sodium formate PDM had lower COD than acetate-based PDMs. The BOD and COD results for acetate-based PDM were consistently lower than those for aircraft deicers, but degradation rates were greater in the acetate-based PDM than in aircraft deicers. Evaluation of BOD results for the sodium formate PDM was confounded by inhibition of microorganisms presumably due to an additive component.

There was no substantial difference between BOD measured in freshwater and BOD measured in marine water tests conducted at 20°C. Tests conducted at 5°C consistently resulted in lower BOD exertion than 20°C tests. The degree of difference between standard and low temperature BOD results varied among tested products. Acetate-based products had greater percentage degradation than glycols at both temperatures. Glycols degraded slower in marine water than in freshwater for low temperature tests, but results were similar in the two water matrices for the 20°C tests.

Traditional BOD test methods did not work well for some alternative FPDs because of two possible reasons. Either microorganisms in the seed inoculums did not adapt well to these FPDs as a food source, or the optimal food-to-organism ratio could not be determined. Other FPDs exhibited lags in BOD exertion in the 28-day tests indicating that the microorganisms needed time to adapt to the food source. For FPDs where the traditional BOD_5 test performed adequately, values ranged from 251 to 1,580 g/kg. For FPDs where the modified test performed adequately, values of BOD_{28} ranged from 242 to 1,540 g/kg. More in-depth research with the specific FPDs is needed to determine methods required to best evaluate the FPDs that did not work well with the methods used in this study, including an evaluation of acclimated inoculums for each of these FPDs.

In addition to the challenges described above, chemicals being tested can exhibit toxicity to the microorganisms in BOD tests. This was the case for the sodium formate PDM formulation used in this study where an additive in the formulation effectively inhibited microbiological activity in the test. This is another case where seed acclimation may be useful to encourage growth of microorganisms that are less sensitive to additive chemicals in the sodium formate formulation.

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