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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · JUNE 2006

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Environ. Sci. Technol. **2006**, *40,* 3195−3202

Characterization of Aircraft Deicer and Anti-Icer Components and Toxicity in Airport Snowbanks and Snowmelt Runoff

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Snowbank samples were collected from snowbanks within a medium-sized airport for four years to characterize aircraft deicer and anti-icer (ADAF) components and toxicity. Concentrations of ADAF components varied with median glycol concentrations from individual sampling periods ranging from 65 to 5940 mg/L. Glycol content in snowbanks ranged from 0.17 to 11.4% of that applied to aircraft. Glycol, a freezing point depressant, was selectively removed during melt periods before snow and ice resulting in lower glycol concentrations after melt periods. Concentrations of ADAF components in airport runoff were similar during periods of snowmelt as compared to active ADAF application periods; however, due to the long duration of snowmelt events, greater masses of glycol were transported during snowmelt events. Alkylphenol ethoxylates (APEO), selected APEO degradation products, and 4- and 5-methyl-1H-benzotriazole were detected in snowbank samples and airport snowmelt. Concentrations of APEO parent products were greater in snowbank samples than in runoff samples. Relative abundance of APEO degradation products increased in the downstream direction from the snowbank to the outfalls and the receiving stream with respect to APEO parent compounds and glycol. Toxicity in Microtox assays remained in snowbanks after most glycol had been removed during melt periods. Increased toxicity in airport snowbanks as compared to other urban snowbanks was not explained by additional combustion or fuel contribution in airport snow. Organic markers suggest ADAF additives as a possible explanation for this increased toxicity. Results indicate that glycol cannot be used as a surrogate for fate and transport of other ADAF components.

Introduction

Aircraft deicing and anti-icing fluids (ADAF) are used at airports during cold weather periods to facilitate safe air travel. The primary forms of ADAF currently in use consist of ethylene glycol, propylene glycol, or diethylene glycol as the freezing point depressant, water, and numerous proprietary additives (the additive package) that vary among different manufacturers and fluid types. Deicers designed to remove ice and snow from aircraft surfaces are referred to as Type I fluids. These fluids are typically diluted with water and heated prior to application. Anti-icers, referred to as Type II and Type IV fluids, are more viscous formulations designed to provide initial deicing and residual anti-icing protection on aircraft during preflight activities and takeoff. Type II and IV fluids are applied directly without dilution.

The fate of spent ADAF is variable. Overspray during initial application will fall to the pavement and nearby surfaces. The ADAF remaining on the aircraft drips off during taxi and holdover activities or shears off during takeoff. Many airports operate ADAF collection systems and subsequently treat or recycle the spent fluids (*1*). A portion of the ADAF flows through storm drains to receiving surface waters, travels to the groundwater system, or is plowed into nearby snowbanks. In snowbanks, it is stored until melting occurs when it is captured by ADAF management systems, or transported to receiving waters. The U.S. EPA has estimated that 35 million kg of ADAF is discharged to receiving waters in the United States annually (*2*).

The primary environmental impacts associated with ADAF discharge to the environment include reduced dissolved oxygen in receiving waters and potential toxicity. Glycols contained in ADAF contain large amounts of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Concentrations of these constituents in airport effluents vary dramatically depending on climate, hydrologic, and ADAF management conditions. Previous field studies have reported concentrations of glycol, 5-day BOD (BOD_5) and COD in airport effluents as high as 39 000 mg/L, 39 000 mg/L, and 60 000 mg/L, respectively (*3*, *4*).

Toxicity due to ADAF runoff has been observed in receiving water samples (*5*−*7*); however, most compounds responsible for this toxicity are proprietary ingredients in the additive packages (*5, 8*), and identities of these compounds are a trade secret. ADAF additive packages contain surfactants used as wetting agents, corrosion inhibitors, flame retardants, polymers that bind ADAF to aircraft surfaces, dyes to help distinguish among ADAF types, foam suppressants, and other additives (*9*). To date, two classes of ingredients included in additive packages have been identified. First, Cancilla et al. (*10*) reported that a mixture of 1H- benzotriazole, 4-methyl-1H-benzotriazole (4-MeBt), and 5-methyl-1H-benzotriazole (5-MeBt) was the primary cause of toxicity to *Vibrio fischeri* (Microtox) in one formulation of Type I ADAF. Subsequent research has verified that benzotriazole and two of its methylated derivatives were present at environmentally significant concentrations in surface water and groundwater receiving ADAF discharges (*6*, *11*). MeBT is used as a corrosion inhibitor and flame retardant in many ADAF formulations. While MeBT contributes to the toxicity of ADAF, it has also been shown that other additive package components con-

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10.1021/es052028m CCC: $33.50
Published on Web 04/12/2006

tribute to toxicity as well (*12*). Second, alkylphenol ethoxylates (APEO), including nonylphenol ethoxylates (NPnEO) and octylphenol ethoxylates (OPnEO), have been identified in 5 of 9 ADAF formulations tested, and have been reported at environmentally significant concentrations in runoff from ADAF operations (*13*). APEO are low-cost nonionic surfactants that reduce surface tension and are characterized by relatively low foaming potential (*14*). These chemicals are of concern because they are potentially toxic to aquatic organisms (*15*, *16*) and have been shown to degrade into several byproducts, including nonylphenol (NP), NP1EO, NP2EO, octylphenol (OP), OP1EO, and OP2EO, that are considered endocrine disruptors (*15*, *16*).

The primary objective of the ongoing research at General Mitchell International Airport (GMIA) is to investigate the effects of ADAF runoff to receiving streams. This research began in 1996 and has focused on BOD and dissolved oxygen in airport outfalls and receiving streams, aquatic toxicity of ADAF and runoff containing ADAF, occurrence and effects of ADAF additives, and the effects of ADAF in airport snowbanks and snowmelt. The objective of this paper is to present results of the characterization of ADAF components and toxicity in airport snowbanks and snowmelt runoff, to compare toxicity and organic chemical content in airport snowbanks with those of snowbanks from other urban land uses, and to provide a preliminary assessment of differences between transport mechanisms of glycols and ADAF additives.

Experimental Section

Snowbank Sampling. The snowbank located on the main terminal ramp snow dump area at GMIA (Figure 1) was sampled six times within the period between February 2000 and March 2003 (Table 1). For each sampling period, the snowbank was surveyed for vertical and horizontal definition and mapped to determine total snow volume. Three to five areas were chosen horizontally along the snowbank for sampling chemistry and water content. For each area, a front-end loader cleared a corridor into the snowbank to allow sampling access. Each corridor was sampled at 1−3 locations. For each location, samples were collected at four vertical sections above the ground, each representing $^1/_4$ of the vertical distance from the ground to the top of the snowbank.

To define water content in the snow, samples were collected using a 5.08 cm coring pipe driven in to a predetermined depth (between 16 and 20 cm). These core samples were collected at the center of each vertical section at every sampling location. Samples were then melted and the water content was measured. Median relative percent difference of duplicate samples was 10.0% ($n = 27$).

The primary sampling design throughout the study included determination of propylene glycol, ethylene glycol, COD, and toxicity from Microtox assays in 18 snow samples at nine sampling locations for each sampling period. This included $^1/_4$ section samples collected at three locations (four samples per location), and one composite sample representing the entire vertical at the other six sampling locations. Glycol mass in the snowbanks was estimated by multiplying the average glycol concentration with the average water content and the total snow volume. During the 2000 sampling period, only the primary sampling design was used. In subsequent years, the primary sampling design was used and study topics were added based on results from the previous year as follows:

During the 2001 sampling period, snowbanks representing industrial, commercial, single-family residential, and multifamily residential land uses, and two reference sites located in a nearby state forest were also sampled as a comparison to the airport snowbank. In addition, gas chromatography/mass spectrometry (GC/MS) analysis for organic molecular

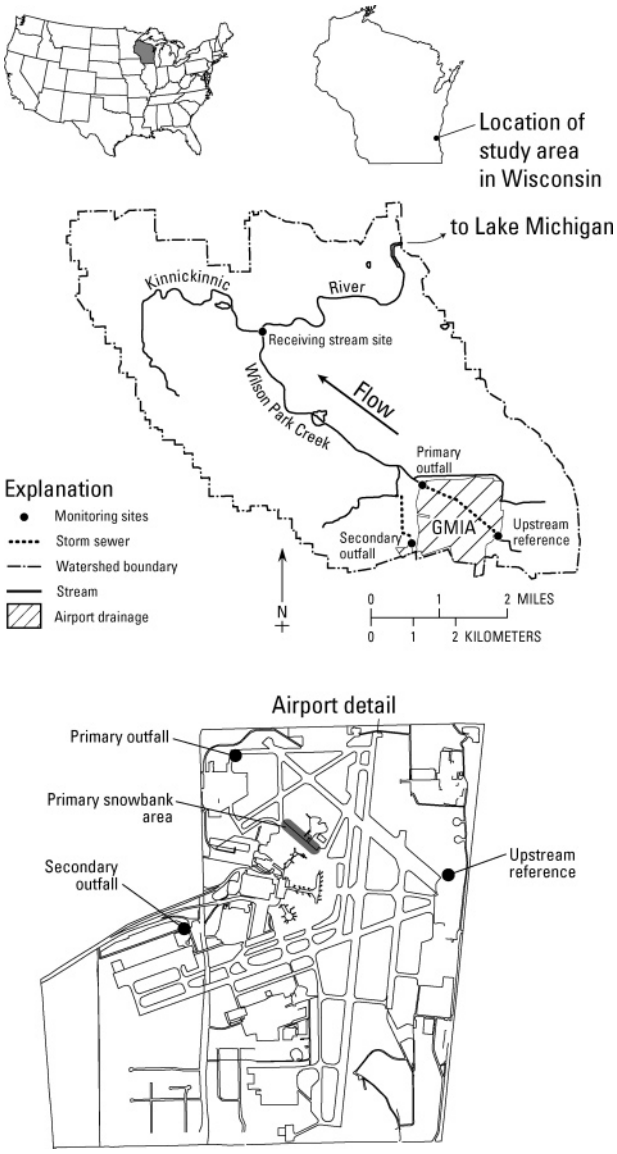

FIGURE 1. Map of field study area, primary airport snowbank, and monitoring stations.

markers and *Ceriodaphnia dubia* bioassays were conducted to characterize the presence of organic chemicals and toxicity in two airport samples (a composite of snow from the top two $^1/_4$ sections from each sampling location and a composite from the bottom two $^1/_4$ sections) and four comparison samples (a composite of industrial and commercial snowbanks, a composite of single- and multi-family residential snowbanks, and two state forest reference samples).

During the 2002 and 2003 sampling periods, the snowbank was sampled on two dates to evaluate temporal changes in the snowbank. During the 2003 sampling period, ADAF additives (APEO and MeBT) were quantified in three airport snowbank samples from both sampling periods. Each sample represented a vertical composite from three sampling locations within one front-end loader corridor.

Runoff Sampling. Water samples were collected at four sites near GMIA: an upstream reference site (drainage area, 2.31 km^2), the primary airport outfall (5.83 km^2), a secondary airport outfall (0.08 km^2), and one receiving stream site (14 km^2) 5.54 km downstream from the airport (Figure 1). The primary outfall site includes flow from the upstream site combined with flow from storm sewers originating in the terminal area (including the main snow dump), taxiways,

TABLE 1. Snowbank Sampling Conditions and Total Glycol Content at General Mitchell International Airport, 2000−2003

	snowbank accumulation period						snow bank data			
sample date	begin date	snowfall (cm)	water equivalent from snowfall (cm)	rainfall (cm)	days with average/ maximum air temperature greater than 0 °C	total glycol applied to aircraft (kg)	snow bank water vol. (m^3)	mean % water content	estimated total glycol content in snowbank (kg)[a]	% of applied total glycol
21-Feb-00	13-Feb-00	28.2	2.59	0.00	0/5	123,000	1,640	60	3,760	3.1
28-Feb-01	11-Dec-00	129	6.43	10.7	10/25	621,000	12,500	67	1,900	0.31
3-Mar-02	2-Mar-02	24.6	2.34	0.00	0/1	49,200	1,080	58	5,610	11.4
13-Mar-02	2-Mar-02	26.9	2.41	0.89	6/8	82,900	429	65	144	0.17
6-Mar-03	4-Mar-03	23.1	0.99	0.00	0/0	52,000	1,910	40	4,690	9.0
11-Mar-03	4-Mar-03	31.8	1.70	0.00	0/2	86,400	1,430	45	8,210	9.5

[a] Glycol content = average glycol concentration × average water content × total snow volume.

and runways. The secondary outfall drains a small area of the airport where most air-cargo activities take place.

Of 36 ADAF runoff events monitored at GMIA between 1997 and 2004, eleven were during snowfall periods, 19 were during other cold-weather precipitation periods, and six were during snowmelt periods. Six of these sampling periods directly coincided with snowbank sampling periods (Table 1). Specific details of the sampling protocol used to collect and process water samples are outlined in Corsi et al. (*17*). Briefly, flow-weighted composite samples were collected throughout each runoff period at each site using refrigerated automatic samplers and Teflon-lined polyethylene sample tubing (model 3700R, Isco Industries, Lincoln, NE). Stream water level was measured every 5 min during periods of increased runoff and every hour during low-flow periods and converted to flow using a log−log relation between water level and flow (*18*).

Inventory of ADAF Application and Recovery. The quantity of ADAF applied by airlines was obtained from the Airport Administration from data submitted by the airlines for an airport-wide compilation of daily ADAF (and glycol) usage. ADAF collected via the airport's ADAF recovery program was monitored by the airport administration to determine operational efficiencies.

Analytical Methods. Methods for determination of glycol, COD, BOD_5, MeBT, and GC/MS analysis methods have all been previously published (*10, 19−22*). Brief details of these and the GC/MS extraction procedures are presented with the Supporting Information. Selected snowbank, outfall, and stream samples from 2003 were also analyzed for the following compounds: APEO (including NP1-16EO and OP1-5EO); the corresponding alkylphenols (AP), NP and OP; and three carboxylated derivatives (APEC), nonylphenoxyacetic acid (NP0EC), nonylphenoxyethoxyacetic acid (NP1EC), and octylphenoxyacetic acid (OP0EC). Methods have been previously published (*23*, *24*), and brief details are provided in the Supporting Information.

Aquatic Toxicity. Bioassays with the water flea, *Ceriodaphnia dubia,* and the marine bacterium, *Vibrio fischeri* (the Microtox test, Azur Environmental, Carlsbad, CA), were used to evaluate toxicity of snowbank and runoff samples (*25*). The endpoint used for *C. dubia* was mortality at 48 h. The endpoint used for Microtox was the percent effect (light reading as a percent difference from the laboratory control sample). Methods for these two tests are provided in the Supporting Information.

Results and Discussion

Snowbank Sampling Conditions. Snowbank samples were collected for four years from the snowbank adjacent to the primary terminal ramp at GMIA (Figure 1). During each year, distinctly different climatic and hydrologic conditions resulted in unique data sets. In 2000 and 2001, samples were collected only one time. In 2002 and 2003, samples were collected two times per year. Rainfall and/or above freezing air temperatures induced substantial melting of accumulated snow prior to the February 2001 sampling period and the second sampling period of 2002 and minor melting before the February 2000 sampling period (Table 1). Significant melting of accumulated snow did not occur prior to the other three sampling periods.

Glycol and Related Constituents. *Snowbanks.* Glycol concentrations, total glycol content, and water content in snowbanks varied between sampling periods and within individual snowbanks depending on conditions during the snowbank accumulation period (Table 1, Figure 2). Propylene glycol was used more extensively than ethylene glycol which is reflected in resulting glycol concentrations. The highest glycol concentrations were detected in samples from the March 11, 2003 sampling period with a maximum total glycol concentration of 16 000 mg/L (COD maximum of 35 500 mg/L) and a median total glycol concentration of 5490 mg/L (COD median of 11 600 mg/L). Samples collected from other snowbanks that had accumulated during periods without rainfall or melting periods also had high glycol and COD concentrations regularly measuring into the thousands of mg/L. The snowbanks that had rainfall or melting during the snowbank accumulation period (the February 28, 2001 and March 13, 2002 sampling periods) had the lowest glycol concentrations, the greatest water content, and the least amount of remaining total glycol content as compared to sampling periods with colder weather and no rainfall (Table 1, Figure 2). Snowbanks from these two sampling periods also had the lowest glycol content as a percent of glycol applied on the aircraft. Some of the glycol removal may be due to biodegradation, but the low temperatures within the snowbank would allow for only very slow degradation rates (*26*). A more likely explanation follows from the fact that glycol is a freezing point depressant and was removed during rainfall and melt periods more readily than snow and ice contained in the snowbanks. This was seen directly when comparing the two sampling periods of 2002 with the two sampling periods of 2003. The 10 days between sampling periods in 2002 had rainfall periods and air temperatures above freezing, causing water percolation through the snowbank and glycol removal. On March 3, 2002, 10.2% of the glycol applied to aircraft was contained in the snowbank while very little glycol was left in the snowbank during the March 13, 2002 sampling period. In contrast, during the 5 days between the sampling periods of 2003, all precipitation was in the form of snowfall and temperatures were below freezing. Glycol content and concentrations increased even though some reduction of water volume in the snowbank occurred between sampling periods.

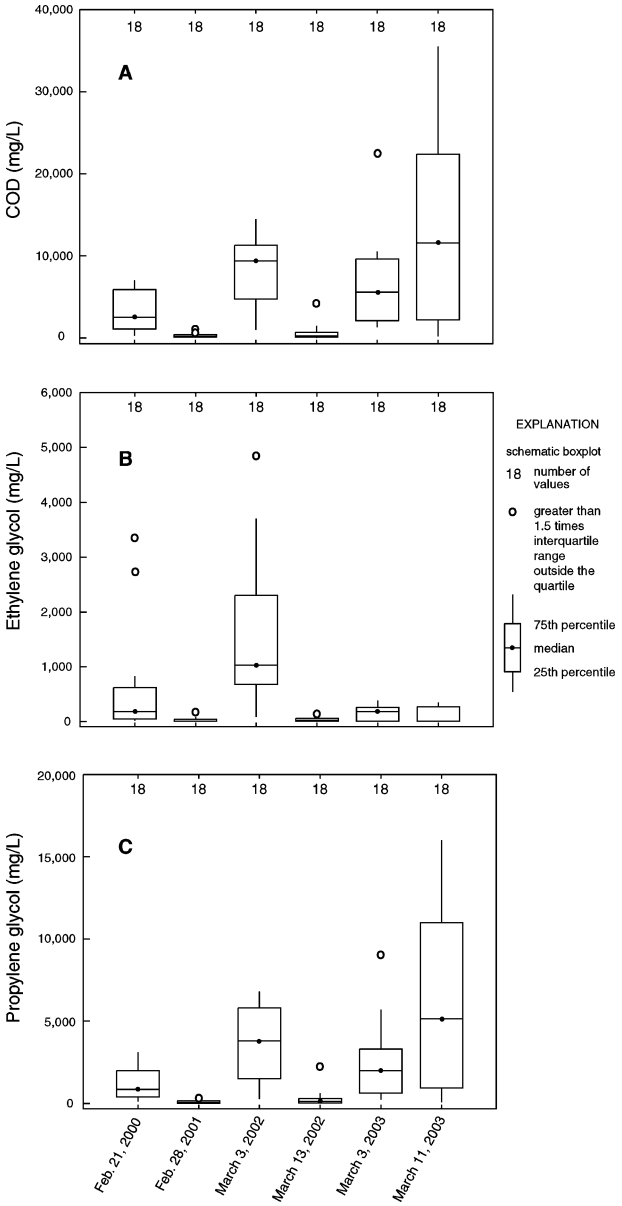

FIGURE 2. Concentrations of propylene glycol, ethylene glycol, and COD in airport snowbank samples collected between February 2000 and March 2003 at General Mitchell International Airport.

Runoff Event Data. Some ADAF was discharged to the stream through airport outfalls during snowfall, freezing rain, or freezing mist, and during snowmelt periods. The exact route, timing, and intensity of ADAF transport to the stream were variable depending on hydrologic conditions, meteorological conditions, the amount of ADAF applied, and the amount of ADAF stored in accumulated snow. Concentrations of ADAF-related constituents at the upstream site were generally very low, with a median concentration of both ethylene glycol and propylene glycol below the detection limit of 18 mg/L (Figure A1, Supporting Information). Event-mean concentrations of glycols at airport outfalls indicate frequent ADAF discharges during cold-weather periods ranging from less than 100 mg/L to greater than 39 000 mg/L with BOD_5 and COD concentrations following the same pattern. Concentrations in samples from the receiving stream site are notably less than those at airport outfalls due to dilution, dispersion, and degradation during transport in Wilson Park Creek.

Concentrations of glycols and related constituents in samples collected during runoff from snowfall and snowmelt events were not significantly different ($p > 0.05$) from samples collected during other ADAF application events except at the secondary outfall (Figure A1, Supporting Information). However, event durations were longest, stormflow volumes from outfalls were greatest, and glycol loadings to the receiving stream were greatest on an event-by-event basis during snowmelt periods as compared to ADAF application periods (Figure A2, Supporting Information). During snowfall periods, flow levels in the outfalls were typically low and much of the ADAF was either collected through the ADAF management system or plowed into snowbanks. This resulted in little ADAF runoff during the snowfall period and an accumulation of ADAF in airport snowbanks. The ADAF discharge from these snowfall periods was delayed and released during melting periods. During other more liquid periods of precipitation requiring ADAF application such as freezing rain or mist, there was more direct discharge of ADAF through the outfalls, and flow levels were greater than those during snowfall periods. Even though concentrations during the more liquid precipitation events were similar to concentrations during snowmelt periods, the longer duration of snowmelt periods resulted in greater masses of ADAF loadings to the outfalls. Also, longer periods of low-level ADAF presence in the stream is of concern with regard to chronic toxicity to aquatic organisms. The shorter-term ADAF application events are a concern with regard to acute toxicity.

TABLE 2. Percent of Applied Glycol Contained in Snowbanks, Recovered through ADAF Management, and Discharged to the Receiving Stream for the 2002 and 2003 Sampling Periods at General Mitchell International Airport

	March 2–3 2002	March 2–13 2002	March 4–6 2003	March 4–11 2003
snowbank	11.4	0.2	9.0	9.5
recovered	25.3	28.4	27.6	26.5
direct runoff	16.3	24	1.7	8.6
unknown	47.0	47.4	61.7	55.3

Mass Balance of ADAF. During the 2002 and 2003 sampling periods, the snowbanks were sampled twice per year. Results from snowbank sampling, runoff sampling, and ADAF management inventories indicated that approximately half of the glycol applied during these periods can be accounted for (Table 2). Results from the first snowbank sampling period each year indicated a nearly constant level of glycol recovery and glycol content in the snowbank, but direct runoff was less during the first 2003 sampling period than during the first 2002 sampling period. This was due to the difference in water content of the two snowfalls. While the two periods had very similar air temperatures, the March 2nd and 3rd snowfall in 2002 had more than twice the water content than that of the March 4th and 5th snowfall in 2003 (Table 1) resulting in greater mobility of ADAF and more runoff at the airport outfall during the 2002 snowfall event.

Sampling results from the second sampling periods of 2002 and 2003 indicated once again that glycol recovery was similar from year to year. Very little glycol was remaining in the 2002 snowbank (due to warm temperatures and rainfall) while glycol content in the 2003 snowbank as a percent of applied glycol was nearly the same as during the first sampling period of 2003. Average daily air temperatures were below freezing during the sampling period in 2003 allowing for less than 10% runoff of glycol to the receiving stream during this period.

A substantial portion of the applied glycol was not accounted for through the monitoring program. There were several potential areas to which ADAF and related glycol could have been transported other than those monitored for this research. First, ADAF can drip from aircraft onto paved areas while taxiing. Second, the ADAF remaining on aircraft

at the time of takeoff is designed to shear from the aircraft and will eventually settle across the airfield and nearby areas. Third, ADAF flows through cracks in pavement and over the side of paved areas and infiltrates into the groundwater system (*6*), and last, much of the ADAF will eventually degrade in the environment (*26*).

ADAF Additives in Snowbanks and Snowmelt. During the 2003 sampling season, selective ADAF additives were quantified in snowbank and snowmelt runoff samples (Table 3). The snowbank samples tended to have higher average concentrations of glycol and most additives (NP, NPnEO, OPnEO, MeBT) than those from the primary outfall, where the melting snowbanks drained, except for several instances of APEO degradation product results (OP, NPnEC, and OP0EC). Degradation of APEO and glycol during storage in the snowbank and/or during melt periods while in transport or possible sorption and deposition of these ADAF surfactant components could have been factors in this result. To investigate further, ratios of the individual APnEO degradation products (NP, NPnEC, OP, OP0EC) to the sum of APnEO parent compounds were computed and compared. For both NPnEO and OPnEO, average ratios increased in the downstream direction from the snowbank to the outfalls and receiving stream sites. Increases in these ratios signify that the relative abundance of individual APnEO degradation products increased from the snowbanks to the receiving stream with respect to the APnEO parent products. Similarly, ratios of APnEO degradation product concentrations to glycol increased in the downstream direction indicating an increase in abundance of APnEO degradation products with respect to glycol concentrations. Conversely, NPnEO parent compounds to glycol ratios decreased and OPnEO parent compounds to glycol concentrations only increased slightly in the downstream direction as compared to the increase in the degradation product to glycol ratios. Whether these differences are due to degradation of APnEO in the snowbanks and/or during transport or whether they are due to selective partitioning to particulate matter, data indicate that glycol monitoring (or monitoring surrogates of glycol such as COD or BOD) cannot be used as surrogates for the fate and transport of additive package components. It has historically been common practice to characterize ADAF runoff by monitoring only glycol, COD, or BOD.

Toxicity. *Microtox Samples.* During each snowbank sampling period, 18 samples were collected for toxicity analysis using the Microtox assay. In addition, samples for Microtox were collected for runoff events at airport outfalls. Microtox analysis was also conducted on a dilution series of propylene-glycol-based Type I ADAF indicating a general increase in toxicity with increasing ADAF concentration. Because not all ADAF used during the sampling period was the Type I formulation used in the dilution series (40% of ADAF used was other formulations), results of this dilution series are used mainly as a common reference between sampling periods. Overall ADAF toxicity in snowbanks would deviate from the dilution series results due to variable toxicity of different ADAF formulations used at this airport. In most snowbank samples, toxicity was equal to or greater than that indicated by the Type I ADAF (Figure 3). Results from three sampling periods that had not been preceded by rainfall or melting periods (Figure 3; C, E, and F) indicated that Microtox toxicity increased with increasing glycol concentration as does the dilution series of Type I ADAF (Spearman's $\rho > 0.5$, $p < 0.05$). Results from the three snowbank sampling periods indicated that samples were more toxic than Type I ADAF and more toxic than samples from the other three sampling periods when compared to glycol concentrations (Figure 3; A, B, and D). The most pronounced differences from Type I ADAF toxicity were the sampling periods that followed rainfall and melting conditions during the snowbank ac-

TABLE 3. Concentrations of Selected Aircraft Deicer and Anti-Icer Additives in Snowbanks and Snowmelt

							NPnEO			OPnEO							
	sampling location	COD mg/L	EG mg/L	PG mg/L	BOD_5 mg/L	NP µg/L	1 µg/L	2 µg/L	3-16 µg/L	OP µg/L	1 µg/L	2 µg/L	3-5 µg/L	NP0-EC µg/L	NP1-EC µg/L	OP0-EC µg/L	4-MeBT µg/L	5-MeBT µg/L
Snowbank samples: Corridor composite concentrations																		
March 6, 2003	corridor A	9,920	219	4,350		8.52	186	157	3,860	0.293	18.7	56	95.4	1.9	2.5	0.3	1,900	1,130
	corridor B	10,200	177	3,600		6.31	168	141	3,530	0.38	21.9	92.4	165	0.99	1.4	0.3	2,150	1,260
	corridor C	9790	223	3,560		2.27	32.4	29.6	174	ND	1.11	2.65	2.91	1.1	1.7	0.056	134	169
March 11, 2003	corridor 2A	18,400	113	9,920		14.7	340	260	6,110	0.85	18.4	58.5	81.5	1.6	2.4	0.32	499	615
	corridor 2B	14,300	223	8,830		13	247	192	3,700	0.963	29.9	120	186	2.5	3	0.51	171	298
	corridor 2C	14,400	306	7,560		3.18	57.5	44.6	474	0.215	1.66	4.34	4.4	1.2	1.6	0.063	<80	<80
Runoff samples: Flow weighted average concentrations																		
March 4–8, 2003	primary outfall	5,600	48	1,900		2.41	17.4	15.4	540	1.2	4.91	13	24.7	2.4	2.8	0.58	103	211
	secondary outfall	20,000	<18	7,300		1.52	7.7	7.17	121	0.227	9.1	28.3	59.1	2	2.5	2.6	103	707
	receiving stream	330	<18	140		ND	0.398	0.385	15.3	ND	0.1	0.629	1.58	0.23	0.42	0.08	<80	<80
March 14–16, 2003	upstream reference	84	<18	<18	16.6	1.22	1.02	1.08	14.8	0.16	0.06	0.189	0.343	0.2	0.32	0.056	<80	<80
	primary outfall	1,300	32	410	738	1.92	8.54	6.17	137	0.495	2.93	9.72	14.9	0.63	0.86	0.37	<80	<80
	secondary outfall	5,800	<18	2,900	>1,000	1.21	13	12.3	526	0.38	6.54	28.4	44.2	1.9	2.3	0.88	248	156
	receiving stream	480	<18	130	201	1.04	2.53	2.33	39.8	0.16	1.07	2.3	3.82	0.32	0.64	0.17	<80	<80

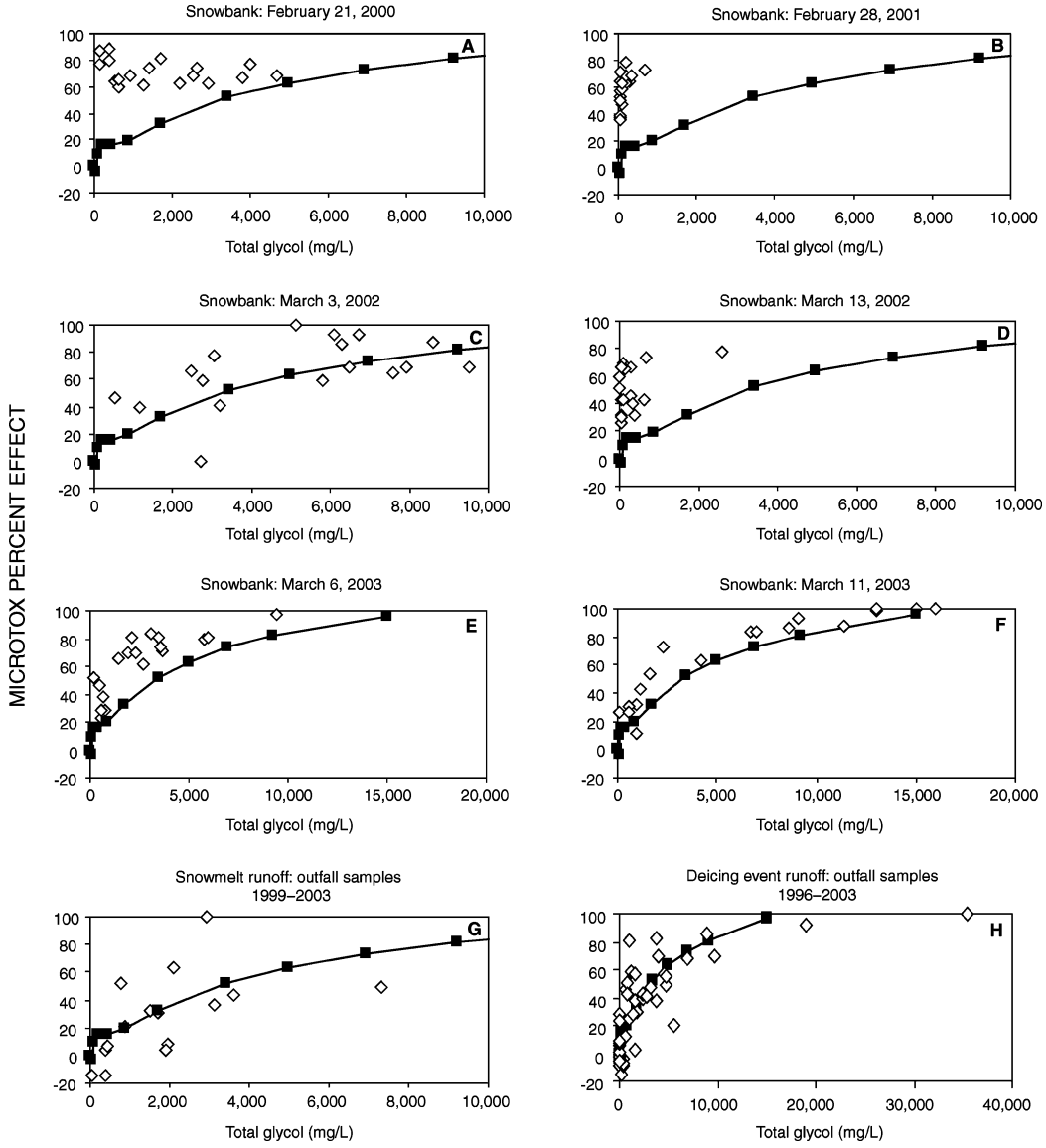

FIGURE 3. Results of Microtox analyses from snowbank samples, snowmelt runoff samples, and ADAF application event runoff samples compared to a laboratory dilution series of Type I ADAF.

cumulation period (Figure 3; B and D). Little glycol was left in these two snowbanks due to removal by rain and meltwater, but a toxic effect was still present. This toxic effect could have been due to non-ADAF related contaminants from the airfield such as fuel, oil, or exhaust from ground vehicles or aircraft. The effect could also have been due to ADAF additives left behind after the glycol had been removed. Comparing results between snowbank sampling periods that followed melting periods and those that did not suggests that additives remaining in the snowbank after glycol has been removed is a more likely cause, but more data are needed to definitively identify the cause of toxicity beyond that from the ADAF dilution series. Results from runoff samples at the two airport outfalls indicated that toxicity increased with increasing glycol concentration (Spearman's $\rho > 0.7$, $p < 0.05$) as does Type I ADAF (Figure 3; G and H). Variability around the dilution series could have been due to different ADAF formulations (with different toxicity characteristics) used within GMIA, different transport mechanisms of glycol and ADAF additive components, degradation of glycol and ADAF additive components, and contaminants from the airfield other than ADAF.

Comparison to Urban Snowbanks. In 2001, urban snowbanks were sampled to compare with toxicity and organic chemical composition in airport snowbanks. Microtox and *C. dubia* acute bioassay results indicate that airport snowbanks exhibited greater toxic effects than urban snowbanks (Table A1, Supporting Information). Of the urban snowbanks, commercial parking lot samples had a greater toxic effect on Microtox, and commercial/industrial composite samples had the greatest effect on *C. dubia* survival than other urban areas and the state forest reference site.

Organic molecular marker analysis, which has been used with atmospheric particulate matter (*27*), was completed for snowbank samples collected in five locations: airport (top and bottom of snowbank), residential roadways, industrial and commercial locations (composited), and a state forest (Table A2, Supporting Information). Organic tracers quantified included tracers for motor oil, combustion, vegetative detritus, biomass burning, and others. Airport samples and the industrial/commercial snow composite showed similar levels of motor oil components (petroleum biomarkers including hopanes and steranes). These compounds are used to track vehicle exhaust, but could also have been from leaking motor oil in snowbank samples. In addition to petroleum biomarkers, polycyclic aromatic hydrocarbons (PAHs) were measured, with the highest concentrations present in the commercial/industrial sample. Contribution of PAHs and

petroleum biomarkers indicate that a portion of toxicity from airport snow was probably from sources similar to those seen in commercial/industrial snow. Snow from state forest samples showed little influence from anthropogenic sources with very low PAH, but contained significant plant wax alkanes and alkanoic acids. According to molecular marker analysis, airport samples do not have additional combustion or fuel contribution that would explain the increase in toxicity over the commercial/industrial snowbanks.

The airport samples contained a series of compounds not present in commercial/industrial, residential, or remote snow tentatively identified as NPnEO (n =2−4). EI GC/MS is not ideal for the quantification of these compounds (but they were analyzed in more detail for the 2003 sampling periods as described above). Still, quantities detected were sufficient to determine that ADAF additives of profile similar to that of snow samples are present in 1 of 4 Type I ADAF formulations tested and 3 of 4 Type IV ADAF formulations. This provides further evidence that ADAF additives were retained in snowbanks after most glycol had been removed during melting and rainfall periods again suggesting that glycol transport mechanisms are different from transport mechanisms of additives.

The combination of toxicity data, organic molecular marker analysis, comparison to urban snowbanks, differences in glycol concentrations in different snowbanks, air temperatures, and precipitation data all point to the possibility that some ADAF additives were retained in the snowbanks to a greater degree than glycol during melting events. Additional research to confirm this possibility should focus on direct additive monitoring in snowbanks and snowmelt before and after rainfall and melting events and comparison to additive profiles in different ADAF formulations.

While much attention in regard to ADAF runoff has been previously focused on glycol and BOD loadings to airport outfalls and receiving streams, it is evident that different transport properties for different ADAF components will be important in order to fully understand fate and transport of ADAF in the environment.

Acknowledgments

Funding was provided by Milwaukee County and the U.S. Geological Survey. We thank the Wisconsin State Laboratory of Hygiene for providing analytical services, Troy Rutter, Todd Stuntebeck, Jeff Steuer, Andrew Mumpy, and Mark Corsentino (USGS), James J. Schauer (Wisconsin State Laboratory of Hygiene and University of Wisconsin), Linda Fellenz, Darin Miller (Kapur and Assoc.), Dean Mericas (CH2M HILL), and Chris Ciecek (Limno-Tech Inc) for their assistance and input. Use of trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Supporting Information Available

Analytical methods, comparison of toxicity in airport snowbanks to urban snowbanks, concentrations of organic tracers in snow samples, schematic boxplots of the concentrations of major ADAF-related constituents in surface water runoff, and schematic boxplots of duration, water volume, and glycol mass loads to the receiving stream during surface water runoff events. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review October 13, 2005. Revised manuscript received February 13, 2006. Accepted March 8, 2006.

ES052028M