Bull. Environ. Contam. Toxicol. (2003) 70:868–875

DOI: 10.1007/s00128-003-0063-8

Bulletin of Environmental Contamination and Toxicology

Detection of Aircraft Deicing Additives in Groundwater and Soil Samples from Fairchild Air Force Base, a Small to Moderate User of Deicing Fluids

D. A. Cancilla,[1] J. C. Baird,[1] R. Rosa[2]

[1] Scientific Technical Services, Western Washington University, Bellingham, WA 98225-9076, USA
[2] 92 CES/CEV 100 West Ent Street, Suite 155, Fairchild AFB, WA 99011, USA

Received: 30 September 2002/Accepted: 30 January 2003

Aircraft deicing and anti-icing fluids (ADAFs) are used heavily world wide, with millions of liters of ADAF entering the environment every year. ADAFs consist primarily of either ethylene or propylene glycol which make up between 80-90% of ADAF mixtures. The remaining components include water and other ingredients such as corrosion inhibitors, thickening agents, surfactants, and fire retardants. The identity of the chemicals making up these components has generally not been made public by the manufactures of ADAFs. Until recently, it was believed that the primary environmental impact related to the release of ADAFs into aquatic systems was the high biochemical oxygen demand resulting from the decomposition of glycols. However, a number of studies have shown that formulated ADAFs are significantly more toxic to aquatic species than glycols alone (Pillard 1995; Fisher et al. 1995; Hartwell et al. 1995; Pillard and DuFrensne 1999; Cornell et al. 2000; Corsi et al. 2001).

In the absence of specific information about the formulated ADAFs, several groups have tried to deduce their composition through a variety of techniques. In 1997, 1H-benzotriazole, 4-methyl-1H-benzotriazole (4-MeBT) and 5-methyl-1H-benzotriazole (5-MeBT) (collectively termed triazoles, Figure 1) were identified as the additives in formulated ADAF mixtures responsible for Microtox activity, a general acute toxicity screen using bioluminescent bacteria (Cancilla et al. 1997). 4- and 5-MeBT were subsequently identified in the groundwater below a major international airport, a large volume ADAF facility, at concentrations approximately 25 times greater than the reported acute EC_{50} values in the Microtox assays (Cancilla et al. 1998). 4- and 5-MeBT were also shown to be present in the tissue of fish exposed to ADAF runoff from a commercial airport (Cancilla et al. 2003).

In general, the United States Environmental Protection Agency (USEPA) considers airports which receive more than 1 inch of snowfall on average and have more than 10,000 operations (i.e. takeoffs and landings) per year (excluding general aviation) to have the potential to perform significant deicing/ anti-icing operations (USEPA 2000). Although the total number of airports performing deicing/anti-icing operations in the U.S. is unknown, it has been estimated that 3957 facilities perform aircraft deicing; of these, 212 meet the stated criteria for

Correspondence to: D. A. Cancilla

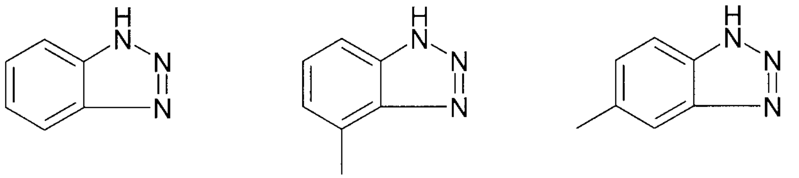

Figure 1. 1H-Benzotriazole, 4-Methyl-1H-benzotriazole (4-MeBT) and 5-Methyl-1H-Benzotriazole (5-MeBT), additives identified in aircraft deicing fluids.

performing significant deicing (USEPA 2000). In a general survey of ADAF use, the volume of applied ADAF per airport ranged from 1,945 L to 8,077,190 L per year; although it is unclear whether these values represent the concentrated or diluted form of ADAF (Type I ADAF is usually applied to aircraft as a 50:50 mixture of water and ADAF).

Much of the evidence for the environmental impact of ADAFs has come from studies conducted at large to mid-size ADAF use facilities. In part, this is due to the perception that only a small number of airports use a majority of ADAF in the U.S.. For example, the American Association of Airport Executives (AAAE) has stated that approximately 90% of deicing operations are performed at 10% of airports (USEPA 2000). For the purpose of this paper, a large ADAF user applies greater than 1,000,000 L, a mid-size user is one that applies between 500,000 and 1,000,000 L, a moderate-size ADAF user applies between 100,000 and 500,000 L of ADAF, and a small-size ADAF user applies less than 100,000 L of ADAF annually. In general, it has been assumed that smaller airports either do not use sufficient ADAF to pose an environmental problem or that dilution and collection practices adequately control the impacts of ADAF released into the environment from these smaller facilities.

This paper presents the results of a study to evaluate whether 4- and 5-MeBT could be detected in soil and groundwater samples from a low to moderate ADAF use facility. As many of the 3745 U.S facilities performing deicing would fall within the small to moderate-size usage group, the detection of ADAF additives would imply that these facilities could also have a potential environmental impact as a result of aircraft deicing activities. Fairchild Air Force Base (Fairchild), located near Spokane, Washington was the site of the study. Fairchild uses approximately 150,000 L of pure ADAF in a typical year, with a majority of the deicing events occurring between the months of November and March. For comparison, General Mitchell International Airport (Milwaukee, WI, USA) considered a mid-sized airport, uses 578,000 to 757,000 L of pure ADAF during a typical deicing season. During the period of this study (December 2000 through August 2001), base personnel had detailed usage records for 117,808 L of pure ADAF. Of this amount, 39,364 L, or 33% of the total, was applied during dry weather deicing events with the remaining 78,444 L being applied during precipitation events. Dry weather deicing is defined as deicing that occurs in the absence of measurable precipitation. Wet weather deicing occurs during precipitation events such as snowfall or freezing rain.

Fairchild has no centralized deicing facility and deicing occurs at locations throughout the flightline, usually at the aircraft parking stubs. The deicer solution is applied to aircraft as a 50:50 mixture of water and ADAF. Depending on weather conditions, anywhere from a few liters to a few hundred liters of the water/ADAF mixture are applied to an aircraft. In general, the excess water/ADAF mixture enters the environment as overspray or drips and is sloughed from the aircraft. As a condition of the Fairchild's National Pollution Discharge Elimination System (NPDES) permit, they are required to cover their storm water collection inlets during dry weather deicing; preventing concentrated ADAF contaminated runoff from exiting the facility via the storm water collection system.

During dry weather deicing, ADAF accumulates on the tarmac and is then collected using a specialized vacuum truck. The collected water/ADAF mixture is stored in an above ground tank for eventual use as a freeze-point depressant in spray mist systems used to control dust on pavement sweeper trucks operating at Fairchild. During wet weather deicing, runoff is allowed to enter storm water inlets and exits the facility through the storm water collection system. Snow and slush containing ADAF is plowed to the edge of the paved surface where it is allowed to eventually melt. The accumulated snow and slush containing ADAF may serve as a reservoir, allowing ADAF to enter soil and groundwater systems well after an actual deicing event.

MATERIALS AND METHODS

All groundwater samples were collected in 1L amber glass bottles while soil samples were collected in 500 mL wide-mouth plastic bottles. Samples were stored at 4 ^{o}C until analyzed. Sample preparation and gas chromatography/mass spectrometry analyses (GC/MS) of groundwater samples has been previously described (Cancilla et al. 1998, Cancilla et al. 2003). For soil analyses approximately 20 g of soil were weighed out and placed in a beaker with 150 mL of methylene chloride. The samples were sonicated for 1 hour with occasional stirring. After sonication the samples were passed through Whatman 1PS phase-separating filter papers (Whatman International LTD., Maidstone, England) to remove particulate matter and excess water. The samples were concentrated to a volume of 1.0 mL and DFBP was added as an internal standard to a concentration of 1.0 mg/L. The concentrated samples were then analyzed by GC-MS.

During the course of this study, groundwater was collected from five monitoring wells located at points near ADAF application (Figure 2). Wells had been constructed in accordance with the Washington Department of Ecology Well

Fairchild Air Force Base Aircraft Deicing and Anti-Icing Fluid Application, November 2000 to April 2001

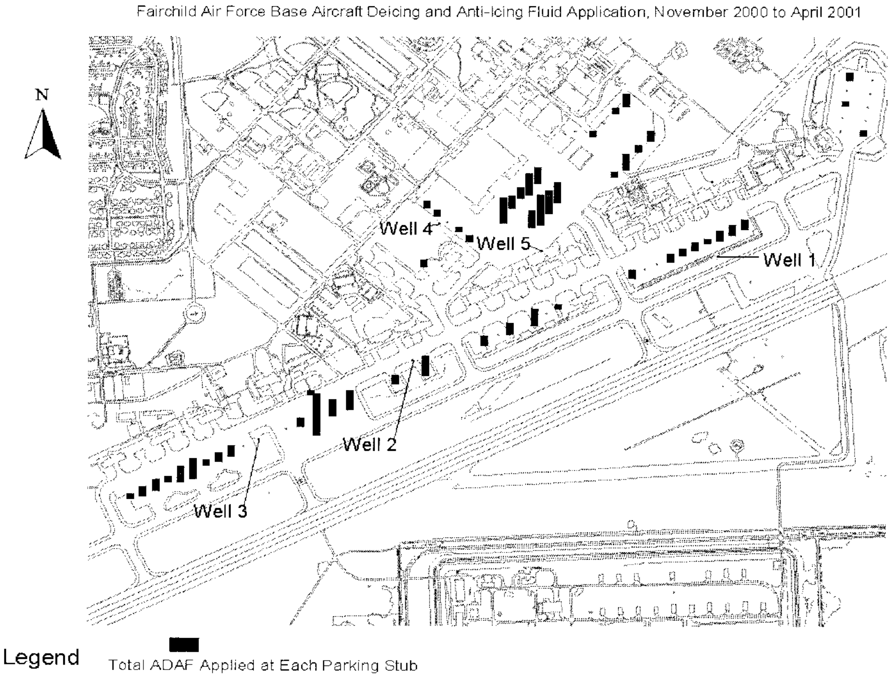

Figure 2. Map of Fairchild Air Force Base with sampling well locations and total deicing activity at each parking location. The size of the bar at each stub is based on the relative amount of ADAF applied at each parking stub.

Construction Standards. Well casings were 2 inch diameter Schedule 40 PVC and installed with a 0.020 in slotted Schedule 40 PVC well screen. The wells were constructed with a bentonite seal in the upper terminus of the well to prevent contaminants entering the system through the well shaft. Wells ranged between 15 and 25 feet deep. At least 5 to 10 casing volumes were evacuated from each well before sampling. Conductivity and pH were monitored and samples were not taken until these parameters were stabilized. The shallow subsurface geology is dominated by relatively coarse glacial sediments that overlie basalt bedrock. The shallow groundwater flow is generally east and east-northeast. The average regional velocity is between 0.11 and 0.2 ft/d. Samples were collected from December 2000 until late August of 2001, for a total of 12 samples per well. Soil samples were collected during several of the sampling visits as weather permitted. Wells 1 and 2 are each located along the taxiway. A minimal amount of deicing activity took place near these wells during the study. The heaviest areas of ADAF application were adjacent to Wells 3, 4 and 5. Well 3 is adjacent to an area of significant deicing activity along the taxiway. Wells 4 and 5 are located near a large, centralized parking and holding area where deicing occurs on a daily basis during the winter months. Most of the snow from this area is plowed off the paved surface and piled near Well 5.

RESULTS AND DISCUSSION

Triazoles were detected most often and in the highest concentrations in samples collected from Wells 3 and 5 (Table 1); locations where the greatest deicing activity occurred. Triazole concentrations ranged from 0.15 mg/L to 3.1 mg/L in Well 3 and were detected on 9 of the 12 sampling dates. Total triazole concentrations ranged from 0.23 mg/L to 0.86 mg/L in Well 5 and were detected on 5 of 12 sampling dates.

Table 1. Triazole analysis of ground water samples from all wells. NA = Sample not analyzed. <DL = Less than the method detection limit (0.08 mg/L). Total MeBT is the sum of the 4- and 5-MeBT isomers.

Date	Well 1	Well 2	Well 3	Well 4	Well 5
	Total MeBT (mg/L)	Total MeBT (mg/L)	Total MeBT (mg/L)	Total MeBT (mg/L)	Total MeBT (mg/L)
12/04/00	NA	<DL	3.1	<DL	<DL
12/18/00	<DL	<DL	0.91	<DL	<DL
01/03/01	0.54	0.32	2.96	<DL	0.78
01/23/01	<DL	0.26	2.7	<DL	0.40
02/13/01	<DL	NA	0.47	<DL	<DL
02/27/01	<DL	<DL	0.33	<DL	0.69
03/20/01	NA	<DL	0.15	<DL	0.23
04/03/01	<DL	<DL	<DL	<DL	0.86
05/01/01	<DL	1.27	2.08	<DL	<DL
06/05/01	<DL	<DL	<DL	<DL	<DL
07/10/01	<DL	<DL	0.89	<DL	<DL
08/21/01	<DL	<DL	<DL	<DL	<DL

The concentrations detected in these wells are within the range known to elicit a positive response in a variety of toxicity assays but are generally well below the effective concentrations where 50 percent of the organisms show an acute toxic response (EC50), usually in the range of 20 to 80 mg/L (Cancilla et al. 2003). The combined triazole concentration (4-MeBT + 5-MeBT) approached the 15 minute Microtox® bacterial assay EC_{50} value (5.91 ± 1.11 mg/L) in Well 3 on several occasions.

Triazoles were detected in 7 of the nine soil samples (Table 2) with the highest levels near Wells 1 (3.93 mg/kg) and 5 (1.03 mg/kg). The frequency of sampling during the study period prevented the detection of pulses of triazoles from short periods of intense deicing activity, and was instead designed to detect seasonal patterns in triazole concentrations. By the time field sampling started, deicing activity had been taking place on site for over a month, and the last recorded deicing activity took place on April 5, 2001. Deicing activity was heaviest in December of 2000 and January of 2001 (Figure 3), and was lighter through February and March of 2001.

Table 2. Triazole analysis of soil samples collected near ground water monitoring wells. ND = Triazoles not detected.

Well and Date	4-MeBT (mg/kg wet weight)	5-MeBT (mg/kg wet weight)
12/04/00		
Well 1	0.72	0.72
Well 1	3.93	ND
Well 2	ND	ND
Well 3	ND	ND
Well 4	0.77	ND
Well 4	1.62	ND
Well 5	1.03	ND
02/13/01		
Well 4	0.73	ND
Well 5	1.73	0.72

The ratio of 5-MeBT to 4-MeBT could be a measure of the age of the ADAF contamination (Table 3). If, as has been suggested by some researchers (Cornell 2002) 5-MeBT is biodegradable and 4-MeBT is recalcitrant, then the 5-MeBT:4-MeBT ratio should approach zero as 5-MeBT decomposes. If this relationship is true, it suggests that the triazole contamination measured at Well 3 is older than the contamination at Well 5. The triazole plume detected at Well 2 may be older still, as 4-MeBT was often detected when 5-MeBT was not. The 5-MeBT:4-MeBT ratios in fresh runoff and in pure ADAF are each higher than those observed in the ground water samples.

Table 3. 5-MeBT:4-MeBT ratio measured in several samples collected at Fairchild

Sample	Average 5-MeBT:4-MeBT Ratio	Standard Deviation	N
Pure ADAF	1.24	-	1
Fresh Runoff	0.91	-	1
Well 5	0.77	0.14	5
Well 3	0.47	0.34	9
Well 2	0.18	0.32	3

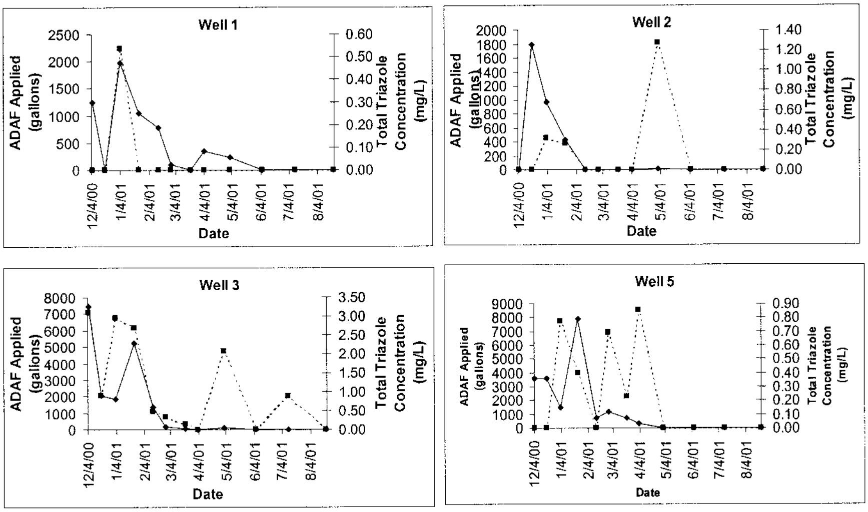

Figure 3. Monthly ADAF applied (in gallons) and total triazole concentration detected (in mg/L) at Well 1, Well 2, Well 3, and Well 5. Triazoles were not detected at Well 4. Total Deicer applied ——◆—— Total Triazole ·········■·········

Although it has been estimated that a large percentage of commercial airports reside near environmentally sensitive areas (USEPA 2000), a vast majority would not be classified as large volume ADAF users (greater than 1,000,000 L). The results of this study have demonstrated that measurable concentrations of triazoles, additives to aircraft deicing fluids, can be detected in groundwater and soil samples collected at a moderate to small ADAF use airport. As many of the environmental studies on ADAFs have occurred at large use airports, the demonstration that deicing chemicals can enter the environment from smaller facilities is significant. ADAFs have been shown to cause adverse environmental impacts on aquatic systems. The potential for smaller airports to negatively impact environmental systems from ADAF use will ultimately depend on a number of factors, such as stormwater management practices. Nonetheless, it is clear that future studies and regulations should also consider ADAF operations at smaller use facilities.

Acknowledgments. The authors would like to thank Steve Burchette of Budinger and Associates for his assistance in the collection and shipping of samples. The Bureau for Faculty Research and the Department of Environmental Science at Western Washington University provided financial and logistical support of this project as did the Civil and Environmental Engineering Group of Fairchild Air Force Base.

REFERENCES

Cancilla DA, Holtkamp A, Matassa L, Fang X (1997) Isolation and characterization of Microtox®-active components from aircraft de-icing/anti-icing fluids. Environ Toxicol Chem 16:430-434

Cancilla DA, Martinez J, Van Aggelen GC (1998) Detection of aircraft deicing/antiicing fluids in a perched water monitoring well at an international airport. Environ Sci Technol 32:3834-3835

Cancilla DA, Baird CJ, Geis SW, Corsi SR (2003) Studies of the environmental fate and effect of aircraft deicing fluids: Detection of 5-methyl-1H-benzotriazole in the fathead minnow (*Pimephales promelas*) Environ Toxicol Chem (in press)

Cornell JS, Pillard DA, Hernandez MT (2000) Comparative measures of the toxicity of component chemicals in aircraft deicing fluid. Environ Toxicol Chem 19:1465-1472

Cornell, J., (2002), Environmental Fate of Aircraft Deicing Fluid Components, PhD Thesis, University of Colorado

Corsi SR, Hall DW, Geis SW (2001) Aircraft and runway deicers at General Mitchell International Airport, Milwaukee, Wisconsin, USA. 2. Toxicity of aircraft and runway deicers. Environ Toxicol Chem 20:1483-1490

Fisher J, Knott M, Turley S, Turley B, Yonkos L, Ziegler G (1995) The acute whole effluent toxicity of storm water from an international airport. Environ Toxicol Chem 14:1103-1111

Hartwell SI, Jordahl DM, Evans JE, May EB. (1995) Toxicity of aircraft de-icer and anti-icer solutions to aquatic organisms. Environ Toxicol Chem 14:1375-1386

Pillard DA. (1995) Comparative toxicity of formulated glycol deicers and pure ethylene and propylene glycol to *Ceriodaphnia dubia* and *Pimephales promelas*. Environ Toxicol Chem 14:311-315

Pillard DA, DuFresne DL. 1999. Toxicity of formulated glycol deicers and ethylene and propylene glycol to *Lactuca sativa*, *Lolium perenne*, *Selenastrum capricornutum*, and *Lemna minor*. Arch Environ Contam Toxicol 37:29-35

U.S. Environmental Protection Agency (2000) Preliminary data summary airport deicing operations (Revised). EPA 821-R-00-016, Office of Water, Washington, D.C., USA. Available on-line at: http://www.epa.gov/ost/guide/airport/airport.pdf accessed September, 2002