Bull Environ Contam Toxicol (2009) 82:265–269
DOI 10.1007/s00128-008-9626-z

Detection of Triazole Deicing Additives in Soil Samples from Airports with Low, Mid, and Large Volume Aircraft Deicing Activities

K. S. McNeill · D. A. Cancilla

Received: 11 September 2008 / Accepted: 26 November 2008 / Published online: 11 December 2008

Abstract Soil samples from three USA airports representing low, mid, and large volume users of aircraft deicing fluids (ADAFs) were analyzed by LC/MS/MS for the presence of triazoles, a class of corrosion inhibitors historically used in ADAFs. Triazoles, specifically the 4-methyl-1*H*-benzotriazole and the 5-methyl-1*H*-benzotriazole, were detected in a majority of samples and ranged from 2.35 to 424.19 μg/kg. Previous studies have focused primarily on ground and surface water impacts of larger volume ADAF users. The detection of triazoles in soils at low volume ADAF use airports suggests that deicing activities may have a broader environmental impact than previously considered.

Keywords Aircraft deicing fluid · Triazoles · Soils · Airports

The extensive use of aircraft deicing and anti-icing fluid (ADAF) in the United States results in the annual release of approximately 80,000,000 L of these fluids directly into surface water surrounding airports (USEPA 2000). Formulated deicers have been found to be more toxic than the main ingredient, either ethylene or propylene glycol, with proprietary additives increasing the overall toxicity of ADAF (Fisher et al. 1995; Pillard 1995). Collectively termed triazoles, 1*H*-benzotriazole (BT), 4-methyl-1*H*-benzotriazole (4-MeBT) and 5-methyl-1*H*-benzotriazole (5-MeBT; Fig. 1), are a class of chemicals historically used in ADAF as corrosion inhibitors and that have been shown to increase the toxicity of ADAF to aquatic organisms (Pillard 1995; Cancilla et al. 1997; Cornell et al. 2000). Although 5-MeBT was found to be more toxic than 4-MeBT (Pillard et al. 2001), 4-MeBT is believed to be more recalcitrant than 5-MeBT in surface water (Weiss and Reemtsma 2005).

Triazoles have previously been measured in surface and ground water surrounding airports, though very few studies have examined the presence of triazoles in airport soils. This, in part, has been due both to the lack of standard analytical and instrumental methodologies for the analysis of triazoles and to the difficulty of obtaining soil samples from active airports. Despite these limitations, triazoles have been detected in airport soils at measurable concentrations (Breedveld et al. 2003; Cancilla et al. 2003). In one case, triazoles were detected in soils 2 years after the cessation of deicing operations (Breedveld et al. 2003). As soils can serve as a potential sink for triazoles and impact the movement of triazoles into ground and surface waters, a better understanding of the extent to which triazoles can be found in airport soils is needed. The purpose of this study was to investigate the extent to which triazoles could be found in soils from airports with differing levels of ADAF use. This paper presents the results for the analysis of triazoles in soils and its application to soil samples collected from low, mid and high ADAF use airports.

Materials and Methods

Soil samples were collected from three airports and represented low (<10,000 L of ADAF annually), mid (100,000 and 500,000 L of ADAF annually) and high volume ADAF use facilities (>500,000 L of ADAF

K. S. McNeill · D. A. Cancilla (✉)
Scientific Technical Services and Huxley College of the Environment, Western Washington University, Bellingham, WA 98225-9076, USA
e-mail: Devon.Cancilla@wwu.edu

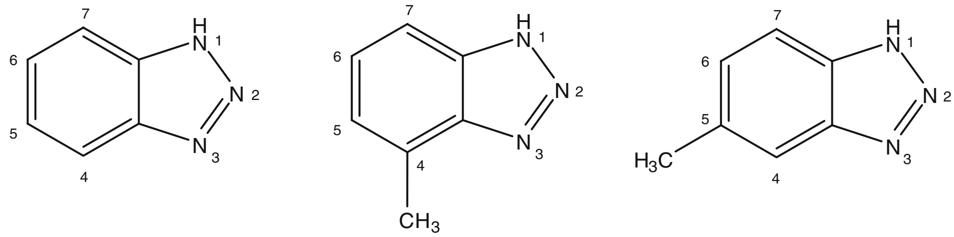

Fig. 1 1*H*-Benzotriazole, 4-methyl-1*H*-benzotriazole and 5-methyl-1*H*-benzotriazole

annually). Samples were collected from the soil layer just beneath the grass roots, and contained parts of both the surface soil and subsoil. All samples were stored in the dark at 4°C until analysis. Soils were dried at 100°C for 24 h prior to extraction. Twenty grams of the dry soil was then fortified to a concentration of 783.5 μg/kg 5,6-dimethyl-1*H*-benzotriazole as a surrogate. Samples were vortexed for 10 min with two 20 mL aliquots of a 1:1 acetonitrile:H_2O (2 mM ammonium acetate) solution and then allowed to sit for 10 min. Samples were then centrifuged for 10 min at 3,500 rpm, after which the supernatant was removed and filtered. Caffeine was added to each 20 mL extract as an internal standard at a final concentration of 389 μg/L. The two 20 mL extractions from each soil sample were then analyzed individually by LC/MS/MS to determine the concentrations of BT, 4-MeBT, 5-MeBT and 4,5-diMeBT and the values from the two measurements summed to obtain triazole concentrations. As commercial standards of 4-MeBT are unavailable, concentrations of 4-MeBT were extrapolated from the response factor of 5-MeBT.

Extracts were analyzed using an Agilent 1100 HPLC system (Agilent, Santa Clara, CA) coupled with an API 2000 MS/MS (Applied Biosystems/MDS Sciex, Foster City, CA). A gradient mobile phase of acetonitrile and H_2O was used with tandem 5.0 μm columns (4.6 mm × 150 mm, Agilent ZORBAX Eclipse XDB-C18). The mass spectrometer was operated in positive ion mode using a TurboIonSpray™ source and multiple reactions monitoring (MRM) scan type. Method detection limits (MDL) were 3.1 μg/kg BT, 2.2 μg/kg 4-MeBT, and 2.2 μg/kg 5-MeBT. Recovery values for BT and 5-MeBT in fortified soil samples were 30.8 ± 4% and 32.1 ± 4%. Because of the low percent recovery in the fortified samples, it is likely that the concentrations measured in the environmental samples are underestimated.

The small ADAF use airport was the Bellingham International Airport (BIA), Bellingham, WA. BIA used 1,250 L of formulated ADAF during the 2006–2007 season. The collection of soil samples from BIA occurred on January 23, 2007, within one day of a deicing event. A second sampling occurred on March 1, 2008, approximately 2 months after the last deicing event of the season. In the first sampling, five soil samples, labeled B1–B5, were collected from sites surrounding the deicing area. Sample B2 was collected from a site where surface runoff from the taxiway and deicing pad pools, and is where snow plowed from those areas is piled. Samples B1 and B3 were collected further from the deicing pad. Sample B4 was collected near the parking area for the deicing truck. Sample B5 was collected across the taxiway from the deicing pad. In the second sampling event, samples were collected from sites B1, B2 and B5. Soils at BIA had an average of 3.56% total organic carbon (TOC) and were determined to be loamy sand, with 78% sand, 19% silt, and 3% clay.

The mid level ADAF use airport was Fairchild Air Force Base (FAFB), located near Spokane, WA. FAFB used a total of 380,000 L of formulated ADAF in the 2006–2007 season. Sixteen samples (labeled F0–F15) were collected at FAFB on June 27, 2007, well after the final deicing events of the season. Samples F1 and F2 were collected from a site that has been minimally used for deicing since 2001, and has not been used at all since 2006. Samples F3, F4, F5, and F6 were collected from a site where snow plowed from a large area used for parking and deicing is piled throughout the winter. Samples F7, F8, and F9 were collected near the same parking and deicing area, though not where snow is piled. Samples F10 and F11 were collected from a site minimally used for deicing, while samples F12 and F13 were from a site that had recently been actively used for deicing. Samples F14 and F15 were collected further from areas of active deicing than all previous samples. A reference sample (F0) was collected away from airport operations at FAFB. FAFB does not have a specific deicing area, so deicing occurs in various locations throughout the airport. In addition to the use of sweeper trucks to clean up ADAF, runoff is collected and discharged using the stormwater system. Soils at FAFB had an average of 1.70% TOC and were determined to be sandy loam, with 64% sand, 33% silt, and 2% clay. Field blanks, travel blanks, and travel spikes from FAFB sample collection were analyzed in triplicate and were considered to be representative of potential contamination during transport of samples from the other airports.

The high use ADAF airport was General Mitchell International Airport (GMIA), located in Milwaukee, WI.

GMIA has regular deicing events throughout the winter, using approximately 1,270,000 L of formulated ADAF during the 2006–2007 deicing season. Five soil samples from GMIA, labeled G1–G5, were collected on September 7 and 8, 2006. Although collected before the first deicing event of the season, the samples were all collected from an area where snow is piled during winter months. Deicing pads are used at GMIA, which also uses sweeper trucks to collect oversprayed ADAF. Soils at GMIA had an average of 4.27% TOC and were determined to be loamy sand, with 85% sand, 13% silt, and 2% clay.

Results and Discussion

The results from the triazole analysis for the BIA soils are summarized in Table 1. The triazole concentrations in the formulated ADAF used at BIA during the study period were 24,324.06 μg/L 4-MeBT and 43,114.43 μg/L 5-MeBT, with a 4-MeBT:5-MeBT ratio of 0.56. BT was not detected in any of the BIA soil samples. Sample B2, which is from an area where deicing runoff collects into puddles, contained the highest level of total triazoles. Sample B1 contained the second-highest level of total triazoles, indicating that triazoles may seep and spread along with water in the soil. It is also possible that the triazoles in sample B1 were present due to overspray, were residually present from previous deicing events, or were present as a result of runway deicing. The increased distance from the deicing pad to samples B3, B4, and B5 resulted in lower triazole concentrations.

The results of the triazole analysis for soil samples from FAFB are shown in Table 2. The concentrations of triazoles in the formulated ADAF used at FAFB during the study period were 160.91 μg/L 4-MeBT and 369.32 μg/L 5-MeBT, with a 4-MeBT:5-MeBT ratio of 0.44. The highest triazole concentrations were in the soil samples collected near the large parking and deicing area (samples F3–F9). Even though the area near samples F1 and F2 had not been used for deicing for over a year previous to sample collection, triazoles were still detected, supporting the findings of Breedveld et al. (2003) of the persistence of triazoles in soil. Samples F12 and F13 contained slightly higher triazole concentrations than samples F10 and F11, as they were collected in an area used more recently, for active deicing. Although, samples F14 and F15 were collected away from areas of active deicing, they contained both 4-MeBT and 5-MeBT. As those sites were adjacent to the tarmac, the triazole concentrations may be indicative of historical exposure and recalcitrance in soils, perhaps from previous deicing activities or the melting of ADAF-contaminated snow into the soil. It is also possible that runway deicers, which can also contain triazoles, were used near those locations. The reference sample (F0) was collected on FAFB property away from airport operations and did not contain detectable levels of any triazole compound. No triazoles were detected in field or travel blank samples.

The results from triazole analysis of GMIA soil samples are summarized in Table 3. Samples of ADAF used during the study period were not analyzed. Except for sample G5, all soil samples contained BT, 4-MeBT, and 5-MeBT, with highest concentrations of 4-MeBT. All of the BT concentrations were lower than the MDL of 3.1 μg/kg BT.

Table 1 Triazole concentrations (μg/kg dry wt) in BIA soil samples

Sample	BT	4-MeBT	5-MeBT	4-MeBT:5-MeBT ratio
January 23, 2007 sampling				
B1	ND	38.31	34.35	1.12
B2	ND	36.92	52.71	0.70
B3	ND	0.36[a]	4.61	0.08
B4	ND	ND	4.05	0
B5	ND	5.88	10.27	0.57
March 13, 2008 sampling				
B1	ND	63.03	44.70	1.41
B2	ND	9.14	22.14	0.41
B5	ND	8.72	16.19	0.54

ND = not detected

[a] Below MDL of 2.2 μg/kg 4-MeBT

Table 2 Triazole concentrations (μg/kg dry wt) in FAFB soil samples

Sample	BT	4-MeBT	5-MeBT	4-MeBT:5-MeBT ratio
F1	ND	16.34	5.37	3.04
F2	ND	12.41	3.77	3.29
F3	1.29[a]	424.19	167.84	2.53
F4	0.86[a]	159.55	70.29	2.27
F5	4.10	88.53	24.46	3.62
F6	0.05[a]	135.46	65.18	2.08
F7	ND	51.96	6.91	7.52
F8	ND	64.77	24.56	2.64
F9	ND	256.17	6.63	38.64
F10	ND	14.64	5.85	2.50
F11	ND	5.84	2.35	2.48
F12	ND	29.79	13.83	2.15
F13	ND	15.58	15.71	0.99
F14	ND	71.86	22.86	3.14
F15	ND	16.81	11.18	1.50
F0	ND	ND	ND	0

ND = not detected

[a] Below MDL of 3.1 μg/kg BT

Table 3 Triazole concentrations (μg/kg dry wt) in GMIA soil samples

Sample	BT	4-MeBT	5-MeBT	4-MeBT: 5-MeBT ratio
G1	0.88[a]	39.26	10.20	3.85
G2	0.41[a]	28.32	4.44	6.37
G3	0.40[a]	18.50	4.75	3.89
G4	2.47[a]	37.49	7.25	5.17
G5	ND	22.96	5.98	3.84

ND = not detected

[a] Below MDL of 3.1 μg/kg BT

The 4-MeBT:5-MeBT ratio in the airport soils generally followed a pattern established in surface and ground water studies, where 4-MeBT is more recalcitrant and 5-MeBT is more biodegradable. In formulated ADAF, the ratio favors 5-MeBT, which degrades over time, shifting the ratio towards 4-MeBT. Only at BIA this relationship was different, with higher levels of 5-MeBT measured in soils. Because degradation of 5-MeBT differs depending on the aerobic or anaerobic conditions of the soil (Benzotriazoles Coalition 2001; Gruden et al. 2001), the relationship between 4-MeBT and 5-MeBT in soils may be difficult to define. It is likely that triazoles degrade differently in soil than in surface and ground water, which was where the relationship was previously determined (Weiss and Reemtsma 2005).

Previous studies have focused on the environmental impacts of deicing at larger airports. This study shows for the first time that triazoles can be detected in soils at small and mid-size airports. Both 4-MeBT and 5-MeBT were present in almost every soil sample from each airport, illustrating the extensive contamination that is likely caused by the use of ADAF and runway deicers. The results also show that triazoles are present in soils up to a year after deicing has ceased. This supports the findings of Breedveld et al. (2003), in which triazoles were detected in soils up to 2 years following the cessation of deicing at the former Oslo, Norway, airport.

The results from this study also support the observations of Corsi et al. (2006) that snow piles impact environmental triazole concentrations and may cause an increase in triazole concentrations in specific areas. Snow cleared from runways, taxiways, and deicing areas are usually piled in specific locations and as the snow melts, triazoles are released into soils along with other ADAF chemicals. At both FAFB and BIA, the highest triazole concentrations were detected in areas where snow is piled or areas that collect runoff from melting snow piles. In areas with snow piles, there is a higher potential for ground water contamination, as the triazoles will percolate through the soils along with melt water.

Overall, the results indicate that triazoles can be detected in soils from airports that use a range of ADAF. Triazoles were able to be detected in soils at airports using from 1,250 to 1,270,000 L of ADAF per year, and at an airport that has less than 5,000 flights per year. This challenges the benchmark of the U.S. Environmental Protection Agency, which considers airports that have more than 10,000 flights per year and an average snowfall of over 1 in. to have a potentially significant environmental impact (USEPA 2000). Although, it is important to understand the environmental impacts of large airports, the results from this study show that small airports can also have an impact on triazole levels in the environment.

Acknowledgments The authors would like to thank Katz Bollinger, Rick Rosa, and Steve Corsi for facilitating airport sample collection. This research was funded through a grant from Huxley College of the Environment at Western Washington University.

References

Benzotriazoles Coalition (2001) Benzotriazoles: category justification and testing rationale. http://www.epa.gov/chemrtk/pubs/summaries/benzo/c13456tp.pdf. Accessed 14 July 2008

Breedveld GD, Roseth R, Sparrevik M, Hartnik T, Hem LJ (2003) Persistence of the de-icing additive benzotriazole at an abandoned airport. Water Air Soil Pollut Focus 3:91–101. doi:10.1023/A:1023961213839

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. doi:10.1897/1551-5028(1997)016<0430:IACOMA>2.3.CO;2

Cancilla DA, Baird JC, Rosa R (2003) Detection of aircraft deicing additives in groundwater and soil samples from Fairchild Air Force Base, a small to moderate user of deicing fluids. Bull Environ Contam Toxicol 70:868–875. doi:10.1007/s00128-003-0063-8

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. doi:10.1897/1551-5028(2000)019<1465:CMOTTO>2.3.CO;2

Corsi SR, Geis SW, Loyo-Rosales JE, Rice CP, Sheesley RI, Failey GG, Cancilla DA (2006) Characterization of aircraft deicer and anti-icer components and toxicity in airport snowbanks and snowmelt runoff. Environ Sci Technol 40:3195–3202. doi:10.1021/es052028m

Fisher DJ, Knott MH, Turley SD, Turley BS, Yonkos LT, Ziegler GP (1995) The acute whole effluent toxicity of storm water from an international airport. Environ Toxicol Chem 14:1103–1111. doi:10.1897/1552-8618(1995)14[1103:TAWETO]2.0.CO;2

Gruden CL, Dow SM, Hernandez M (2001) Fate and toxicity of aircraft deicing fluid additives through anaerobic digestion. Water Environ Res 73:72–79. doi:10.2175/106143001X138714

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. doi:10.1897/1552-8618(1995)14[311:CTOFGD]2.0.CO;2

Pillard DA, Cornell JS, Dufresne DL, Hernandez MT (2001) Toxicity of benzotriazole and benzotriazole derivatives to three aquatic species. Water Res 35:557–560. doi:10.1016/S0043-1354(00)00268-2

U.S. Environmental Protection Agency (USEPA) (2000) Preliminary data summary: Airport deicing operations. EPA 821-R-00-001. Office of Water, Washington DC., USA

Weiss S, Reemtsma T (2005) Determination of benzotriazole corrosion inhibitors from aqueous environmental samples by liquid chromatography-electrospray ionization-tandem mass spectrometry. Anal Chem 77:7415–7420. doi:10.1021/ac051203e