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Detection of Aircraft Deicing/ Antiicing Fluid Additives in a Perched Water Monitoring Well at an International Airport

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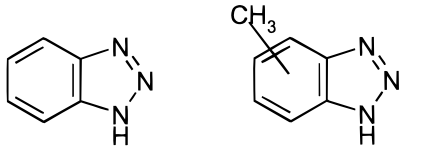
Tolyltriazoles have recently been shown to be the primary agents in aircraft deicing/antiicing fluids (ADAFs) responsible for acute Microtox activity. However, little is known about the fate and effect of these compounds in the environment resulting from airport deicing activities. This research communication describes the first evidence that constituents within ADAFs, other than glycols, are present in subsurface water samples from a major North American airport at environmentally significant concentrations. These concentrations are approximately 25 times higher than the reported EC50 values in Microtox assays.

Introduction

It has been estimated that approximately 52 million L of aircraft deicing/antiicing fluids (ADAFs) are used in a typical year in North America (*1*). Virtually every airport in North America conducts some level of aircraft deicing at some point during the year. Until recently, the primary environmental concern related to aircraft deicing has been the high biochemical oxygen demand (BODs) in waters receiving airport stormwater discharge. High BOD levels have been attributed to the high concentrations of glycols present in these fluids, which range between 50 and 90% ethylene, propylene glycol, or combinations of these and other glycols. Regulations limiting ADAF release into the environment have focused almost exclusively on glycol levels released into the environment. For example, the Canadian Environmental Protection Act (part IV, glycol guidelines, Gazetted February 5, 1994) stipulates an end-of-pipe limit for total glycols of 100 ppm (mg/L) (*2*).

Recently, a number of studies have shown significant toxicological effects of ADAFs that appear to be unrelated to the presence of glycols. These effects are believed to be related to additives in ADAF formulations (*3*−*5*). Additives, which make up between 10 and 20% of the ADAF formulations, include wetting agents, corrosion inhibitors, surfactants, dyes, thickeners, and other agents (*6*). Unfortunately, the exact formulation of ADAFs are proprietary, making it difficult to relate environmental effects to the presence of specific chemical agents. Evidence of the proprietary nature of these fluids can be seen by evaluating Material Safety Data Sheets (MSDS), which list most constituents other than the glycols as proprietary compounds.



I. Benzotriazole II. Tolyltriazole

FIGURE 1. Benzotriazole (I) and tolyltriazole (II).

Recently, a bioassay-directed isolation of ADAF fluids using a standard Microtox acute toxicity assay allowed the identification of a class of ADAF additives known as tolyltriazoles (Figure 1) (*7*). In particular, benzotriazole and methyl substituted benzotriazoles, have been identified. Tolyltriazoles, commonly used as corrosion inhibitors in virtually all antiicing and engine coolant formulations, have also been used in a number of other applications, such as automobile antifreeze mixtures, cooling towers, and photographic development (*7*). Various toxicological studies on tolyltriazoles have shown that these compounds have high to moderate toxicity (*8*−*10*).

This research communication describes the first evidence that tolyltriazoles are present in subsurface water samples from a major North American airport at environmentally significant concentrations as a result of aircraft deicing.

Materials and Methods

Sample Collection. Samples were collected from a perched water monitoring well located near a passenger loading bridge on the main apron of a major North American international airport. The well is used as a sampling location to measure glycol concentrations as part of the airport's glycol and environmental compliance efforts. Samples for tolyltriazole analyses were collected from a water level of approximately 15 feet in July 1997. At least 20 L of purge water were allowed to pass through the well before samples were collected. Four separate 500 mL amber bottles were used to collect samples, which were then placed in a cooler containing ice packs and subsequently in a refrigerator at 4 °C until analyzed.

Sample Preparation and Analysis. An abbreviated method following that described by Cancilla et al. (*7*) was used for sample preparation and analysis. In brief, 25 mL of the sample water was placed into a 100 mL separatory funnel and extracted 3 times with 10 mL of methylene chloride. The methylene chloride was then concentrated to 1 mL under a steady stream of nitrogen. Two microliters of the concentrated extract were then used for chromatographic analysis using a flame ionization detector for initial detection and quantitation and mass spectrometry for confirmation.

Microtox Analysis. Microtox analysis was performed using the standard test methods recommended by Azur Environmental (*11*) with a starting dilution of 6.8% (sample/distilled water). Briefly, toxicity is measured as a reduction in light production in treated versus untreated bioluminescent bacteria.

Results and Discussion

Tolyltriazoles were positively identified in the well water samples collected from a major North American international airport. The presence of these compounds was supported by matching retention times from laboratory-prepared standards as well as mass spectral confirmation. As the initial

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TABLE 1. Estimated Concentrations ppm (mg/L) of Benzotriazole, 5-Methylbenzotriazole, and Isomeric Methylbenzotriazole Against a 10 Mg/L Standard Response by Area

compd	10 ppm standard area	av sample area[b]	estimated concn (ppm)
benzotriazole	15 989	202 533	126
5-methylbenzotriazole	34 176	57 176	17
methyl substituted benzotriazole[a]	34 176[a]	678 926	198
5,6-dimethylbenzotriazole	20 530	not detected	

[a] Estimation based upon response of standard 5-methylbenzotriazole. [b] Average of two samples.

TABLE 2. Microtox IC50 Values at 5 and 15 Min for Four Samples Collected from a Perched-Water Monitoring Well[a]

sample	5 min IC50 (%)	95% C. L. (%)	15 min IC50 (%)	95% C. L. (%)
1	0.24	0.21−0.27	0.27	0.25−0.30
2	0.21	0.20−0.22	0.27	0.26−0.28
3	0.23	0.22−0.25	0.25	0.24−0.28
4	0.25	0.21−0.29	0.23	0.21−0.25

[a] IC50 = the inhibition concentration causing 50% decrease in light production at 5 and 15 min. C. L. = confidence limits.

goal of this project was to detect the presence of tolyltriazoles and not to rigorously quantitate tolyltriazole concentrations, only estimated concentrations relative to the area response of a 10 mg/L (ppm) standard can be presented at this time. Table 1 provides these data.

These concentrations appear to be two to three times higher than the reported Microtox EC 50 values. Glycol levels from the well were previously reported to be 24 410 mg/L in samples collected in April of 1996. Glycol levels were not measured in the current study.

Microtox analysis of the groundwater samples showed the samples to be potentially extremely toxic, with IC50 values (the inhibition concentration causing 50% decrease in light production) ranging between 0.21 and 0.25% for each of the four samples (Table 2). The starting groundwater concentration was 6.25%.

It should be noted that the Microtox-toxicity of the groundwater samples can only be circumstantially linked to the presence of tolyltriazoles at this time. However, the presence of these compounds in groundwater samples and the previous demonstration of their toxicity at significantly lower levels suggest that these compounds could contribute to the overall Microtox-toxicity of the samples.

This preliminary work has demonstrated for the first time that tolyltriazoles, constituents present in aircraft deicing/antiicing fluids, can be detected in the perched water table beneath an international airport. A bioassay-directed fractionation of this water sample is currently underway in an attempt to identify the Microtox-active component(s). Further work is also underway to develop the appropriate analytical methodologies necessary to accurately evaluate the concentrations of these compounds in the environment.

As tolyltriazoles have become a commonly used class of corrosion inhibitors in automobile engine coolants and other products, it is postulated that tolyltriazoles will also be found as environmental contaminants in locations other than airports as a result of past and current disposal practices of these types of coolants and products.

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