Environmental Management

Benzotriazole concentrations in airport runoff are reduced following changes in airport deicer formulations

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Abstract

A comparison of the presence of additives in airport deicers commonly used in the United States and in airport runoff was conducted with data collected before and after changes in deicer formulations. Three isomers of benzotriazoles (BTs)—4-methyl-1H-benzotriazole (4-MeBT), 5-methyl-1H-benzotriazole (5-MeBT), and 1H-benzotriazole (1H-BT)—are corrosion inhibitors added to some formulations of airport deicers and are reported to be a source of aquatic toxicity in streams receiving airport runoff. Concentrations of BT in aircraft deicers and anti-icing fluids (ADAF) were reduced over time but were not reduced in potassium acetate airfield-pavement deicer material (PDM) that was used throughout the study period. Streams receiving runoff from Milwaukee Mitchell International Airport, Milwaukee, Wisconsin, USA, were monitored from 2004 to 2019 for BTs, with concentrations of 4-MeBT varying from <0.35 to 4600 µg/L, 5-MeBT varying from <0.25 to 6600 µg/L, and 1H-BT varying from <0.25 to 150 µg/L. Median 4-MeBT concentrations at sites downstream from the airport decreased by approximately 74%, 5-MeBT by 69%, and 1H-BT by 82% following reduction in BTs in ADAF formulations, resulting in a reduction in the potential for aquatic toxicity in receiving streams. A change in residuals from regression analysis between freezing point depressants and BTs indicate that the reduction in BT concentrations in airport runoff was a result of BT reduction in ADAF formulations, but PDM may still be a substantial source of BTs in airport runoff. Because BTs are a source of aquatic toxicity in airport deicers, the reductions in BTs in the common deicers observed in this study can be used to demonstrate the potential for a reduction in the effects to aquatic organisms in airport runoff, resulting in greater likelihood of meeting aquatic toxicity requirements in airport stormwater permits, and potentially driving airports, airlines, and permit holders to advocate further reduction or elimination of BTs and other harmful contaminants in airport deicers. *Integr Environ Assess Manag* 2022;18:245–257. Published 2021. This article is a U.S. Government work and is in the public domain in the USA. *Integrated Environmental Assessment and Management* published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC)

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INTRODUCTION

Airports worldwide use chemical deicing and anti-icing agents to clear snow and ice from aircraft, runways, taxiways, and other paved surfaces during periods of freezing precipitation. Previous research has demonstrated that it is not uncommon for airports to release deicers to receiving water bodies, and these chemicals can cause detrimental ecological effects (Cancilla et al., 1997; Corsi, Geis,

Loyo-Rosales, & Rice, 2006; Corsi et al., 2009; Fisher et al., 1995; Hartwell et al., 1995). Since these studies, deicer formulations have been modified with manufacturers indicating a removal of the most toxic components, presenting potential widespread water quality improvements, but verification of these changes in deicer formulations and airport runoff have not been demonstrated.

The most commonly used aircraft deicer fluids, approved by the United States Federal Aviation Administration, include Type I deicers used for removing ice, frost, and snow from aircraft surfaces, Type IV anti-icers, which are more viscous and are applied to prevent the formation of ice and snow on aircraft, and liquid and solid pavement deicers. Liquid pavement deicers are often applied directly to airport runways, taxiways, and other paved surfaces in advance of a freezing precipitation event to prevent the adhesion of ice and snow to the pavement and facilitate physical removal of snow and ice (Corsi et al., 2009). Solid pavement deicer is applied directly to penetrate existing snow and ice, often

followed by additional application of liquid pavement deicer to reduce adhesion of ice to paved surfaces (Corsi et al., 2009).

Aircraft deicing and anti-icing fluids (ADAF) are primarily composed of freezing point depressants, such as propylene glycol-, ethylene glycol-, and diethylene glycol-based fluids, water, and lower concentrations of various additives to enhance performance, such as corrosion inhibitors, surfactants, anti-foaming agents, thickeners, dyes, flame retardants, and pH buffers (National Academies of Sciences Engineering and Medicine [NASEM], 2009). Airfield-pavement deicer materials (PDM) consist of organic salts as the freezing point depressants, such as potassium acetate (liquid), sodium acetate, and sodium formate (solids) as well as additives such as corrosion inhibitors and anti-caking agents.

Aircraft deicing and anti-icing fluids and PDM (collectively referred to as deicers) can cause negative effects on aquatic ecosystems when released into the environment, including biochemical oxygen demand (BOD) and aquatic toxicity (Corsi, Booth et al., 2001; Corsi, Hall et al., 2001; Corsi et al., 2009; Fisher et al., 1995; Hartwell et al., 1995; Kent et al., 1999). Stormwater permits for airports that apply deicers commonly include requirements for BOD and aquatic toxicity (US Environmental Protection Agency, 2012). Freezing point depressants, such as propylene glycol, ethylene glycol, potassium acetate, sodium acetate, and sodium formate are high in BOD and chemical oxygen demand (COD), which can result in decreased dissolved oxygen levels in receiving waters (Corsi, Booth et al., 2001; Corsi et al., 2009). Further, additives in ADAF and the freezing point depressants in PDM have been implicated as the primary components of deicer formulations that contribute to aquatic toxicity in streams receiving airport runoff (Corsi, Geis, Loyo-Rosales, & Rice, 2006; Corsi et al., 2009; Hartwell et al., 1995; Pillard 1995).

Although manufacturers of deicer products maintain proprietary formulas for the additive packages, researchers have identified the corrosion inhibitor benzotriazoles (BTs) and surfactants as additives of concern with regards to aquatic toxicity (Cancilla et al., 1997; Cornell et al., 2000; Corsi, Geis, Loyo-Rosales, & Rice, 2006; Li, 2013; NASEM, 2009; Pillard et al., 2001; Seeland et al., 2012). Reformulation to reduce additives responsible for aquatic toxicity would reduce effects on aquatic organisms in airport runoff, providing a greater likelihood of meeting aquatic toxicity requirements in stormwater permits.

The three BT isomers known to be present in deicers and airport runoff are 4-methyl-1H-benzotriazole (4-MeBT), 5-methyl-1H-benzotriazole (5-MeBT), and 1H-benzotriazole (1H-BT). Studies have shown BTs to be a source of acute toxicity to microorganisms (Cancilla et al., 1997; Corsi, Geis, Loyo-Rosales, & Rice, 2006; Pillard et al., 2001) and have been found in ecologically significant concentrations in surface water and groundwater receiving airport runoff (Cancilla, 1998; Cancilla et al., 2003). Owing to environmental concerns, some

manufacturers indicated that BTs would be phased out of some deicer formulations. Previous studies have emphasized the potential detrimental effects of deicer components before these formulation changes (Cancilla, 1998; Corsi et al., 2003, 2009, Corsi, Geis, Loyo-Rosales, & Rice, 2006; Corsi, Geis, Loyo-Rosales, Rice, Sheesley et al., 2006), but information verifying these reductions in deicers and airport runoff is currently lacking.

The overall objectives of this study are to (1) define concentrations of BT isomers over time in deicers commonly used at the Milwaukee Mitchell International Airport (MKE; previously known as General Mitchell International Airport [GMIA]) and throughout the United States, (2) monitor concentrations of BT isomers in airport runoff over time from the mid-2000s through 2019, (3) determine if concentrations of BT have changed in airport runoff during the monitoring period, and (4) evaluate the implications of runoff containing BTs on aquatic life.

METHODS

Two lines of evidence were used to evaluate changes in BT over time. First, deicer formulations were analyzed for BT content and compared with BT content in deicers from previous studies published in 2006 and 2009 (Corsi, Geis, Loyo-Rosales, & Rice, 2006; NASEM, 2009). Deicer formulations were chosen to represent most of the deicer products used at MKE and to represent common deicers used throughout the United States at airports where deicing operations are necessary for safe travel. Second, a case study was conducted to quantify BT in airport runoff over time to verify that changes in deicer formulations resulted in a corresponding change in water quality.

Deicer formulations

Deicers used at MKE were compared with a recent list of current-use deicers and verified to represent commonly used products throughout the United States (Mericas et al., 2020). Formulated Type I, Type IV, liquid pavement, and solid pavement deicers and anti-icers were collected on site by airport personnel directly from storage at MKE. After sample collection, samples were placed on ice and delivered to the laboratory within 24 h for 4-MeBT, 5-MeBT, and 1H-BT analysis.

Case-study area

Water samples were collected from four sampling locations near MKE, Milwaukee, Wisconsin, USA, from 2004 through 2019: one upstream reference site, two airport outfalls, and one receiving stream site 5 km downstream from the airport (Figure 1; Table 1). A 2.31 km^2 section of the headwaters region of Wilson Park Creek was sampled as an upstream reference site (Figure 1). This site drains a primarily urban (residential and commercial) area, as well as a small part of the runway and US National Guard facility at MKE, resulting in the potential for small amounts of airport runoff to reach the site. Two airport outfalls that drain to Wilson Park Creek were sampled to characterize runoff from
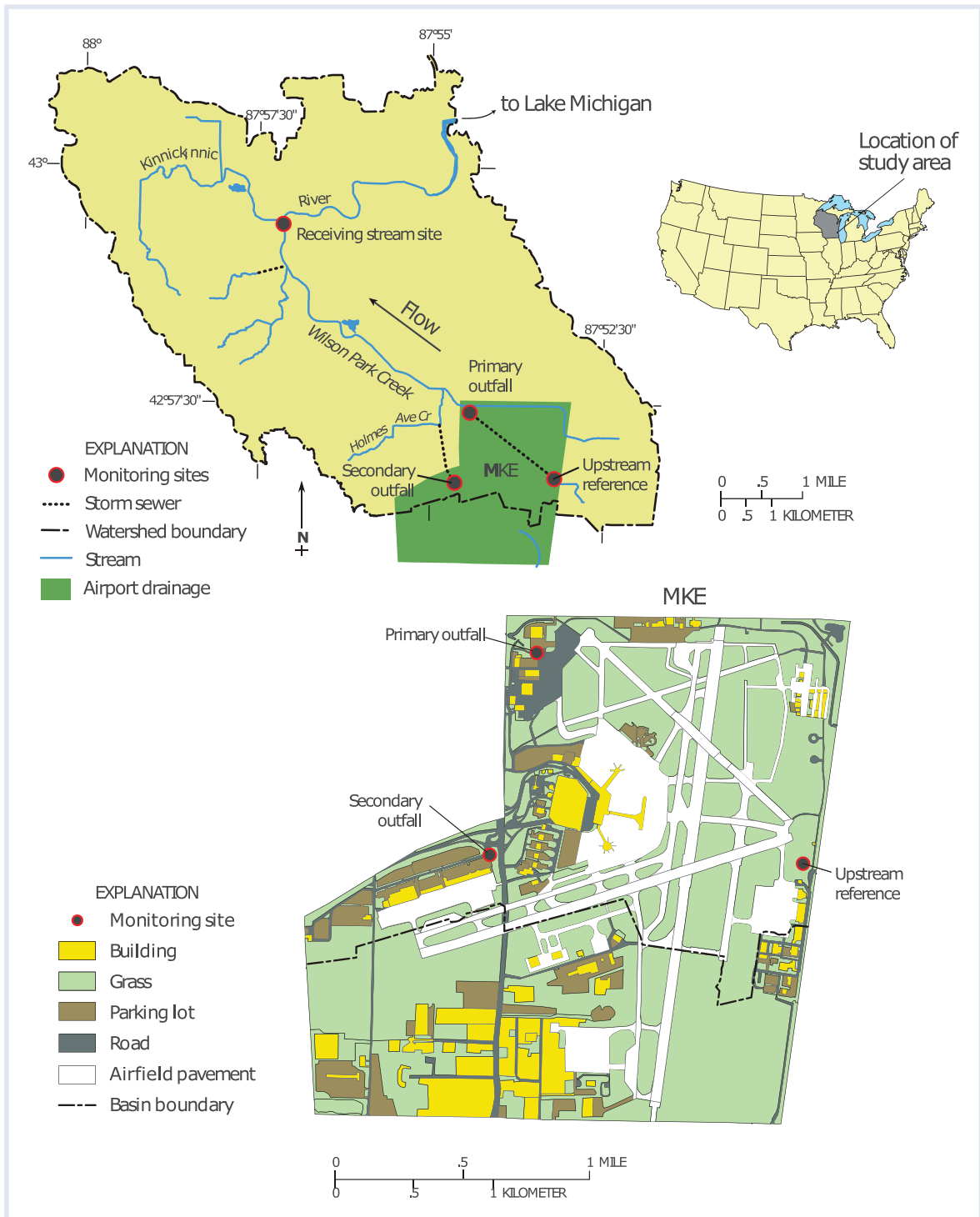
FIGURE 1 Study area and sampling locations near Milwaukee Mitchell International Airport (MKE), Milwaukee, Wisconsin. Revised from Corsi et al. (2009)

the airport. The primary outfall site (Figure 1) has a drainage area of 5.83 km^2 (3.52 km^2 within the airport) and receives flow from the upstream site as well as flow from storm sewers that drain the terminal area and some taxiways and runways. The secondary outfall drains a 0.08 km^2 area of the airport where most air-cargo activities take place discharging into Holmes Avenue Creek, which flows into

Wilson Park Creek approximately 0.08 km downstream from the primary outfall. The receiving stream site was monitored to characterize water quality effects (Figure 1) on Wilson Park Creek just above its confluence with the Kinnickinnic River, 5.54 km downstream from the airport and with a drainage area of 29.37 km^2. Between the airport and receiving stream site, the channel alternates between a

TABLE 1 Sampling location information for sampling sites near Milwaukee Mitchell International Airport, Milwaukee, Wisconsin

Sampling location name	USGS site identification number	Site purpose	Drainage area (km²)	Mean flow (m³/s)
Wilson Park Creek at GMIA[a] Infall at Milwaukee, Wisconsin	040871473	Upstream reference	2.31	0.01–0.04[b]
Wilson Park Creek at GMIA[a] Outfall #7 at Milwaukee, Wisconsin	040871475	Primary outfall	5.83	0.06–0.13[c]
Holmes Ave Creek Tributary at GMIA[a] Outfall #1 at Milwaukee, Wisconsin	040871476	Secondary outfall	0.08	0.00034–0.0025[b]
Wilson Park Creek at St. Luke's Hospital at Milwaukee, Wisconsin	040871488	Downstream receiving stream	29.37	0.26–0.57[b]

[a]Milwaukee Mitchell International Airport (MKE) was previously abbreviated as GMIA.
[b]Range of mean flows over the sampling period of November–April in 2004–2018.
[c]Range of mean flows over the sampling period of November–April in 2006–2018.

concrete-lined channel and an earthen channel bottom. Immediately downstream of this site, Wilson Park Creek drains into the Kinnickinnic River, flows for 4.33 km to the Kinnickinnic River Estuary, and ultimately drains to the Milwaukee Harbor and into Lake Michigan.

Surface-water sampling

Surface-water quality sampling was conducted during cold-weather periods, November through April during the years 2004–2019. Composite samples were collected and processed during runoff periods using methods previously described (Corsi, Booth et al., 2001). Briefly, refrigerated automatic samplers (model 3700R; Isco Industries) and Teflon lined polyethylene sample tubing were used at each site to collect flow-weighted composite samples. Following sample collection, samples were placed on ice, split for separate chemical analyses, and then filtered (if required for the analyses described below). Unfiltered water samples for 4-MeBT, 5-MeBT, and 1H-BT were collected in clean baked amber 500 ml borosilicate glass bottles. Samples collected for propylene glycol were filtered (0.2 μm CA filter media, 25 mm polypropylene capsule syringe filter; Whatman) into two individual 40 ml plastic bottles. Potassium samples were collected in 250 ml plastic bottles and acidified with nitric acid. Samples were then delivered to the Wisconsin State Laboratory of Hygiene (WSLH) within 24 hours.

Chemical analysis

All chemical analyses were conducted at the WSLH. For BT isomer samples analyzed before water year 2007 (a water year is the period between 1 October of one year through 30 September of the next and designated by the calendar year in which it ends; e.g., 1 October 2006 through 30 September 2007), WSLH method ESS ORG 1614 was followed: a 500 ml aliquot of sample was placed in a 1 L separatory funnel, and 2 ml of 50% hydrochloric acid was added and extracted three times with 50 ml of methylene chloride. The three fractions were combined, 2 ml of methanol was added, and the solution was concentrated to 2.0 ml. The extract was then injected into a gas chromatograph equipped with a flame ionization detector, and the response of the sample was compared with standards prepared in methanol. A minimum of five levels of calibration was desired. For samples analyzed in water year 2007 and later, WSLH method ESS ORG METHOD OC16151 was followed. Water samples were filtered with 0.22 μm pore size hydrophilic polytetrafluoroethylene (PTFE) syringe filters (Restek Part Number 26144, or equivalent) and then analyzed by high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS). Separation of the analytes was achieved using isocratic elution chromatography. After elution from the HPLC column, analysis was done using a turbo ion spray triple quadrupole mass spectrometer in the positive ionization mode. The detection limit for BTs changed

from 40 µg/L before water year 2007 to 0.35 µg/L (4-MeBT) or 0.25 µg/L (5-MeBT and 1H-BT) after water year 2007.

Propylene glycol samples were analyzed by gas chromatograph and flame ionization detector according to US Environmental Protection Agency Method 8015A (US Environmental Protection Agency, 1992). Reporting levels for propylene glycol varied from 10–20 mg/L. Samples collected for potassium were analyzed by inductively coupled plasma-atomic emission spectrometry according to US Environmental Protection Agency Method 200.7 (US Environmental Protection Agency, 1994).

Water quality data from this study are archived in the US Geological Survey National Water Information System (NWIS; U.S. Geological Survey, 2019) and provided in the supplemental information (Table S1).

Quality assurance

Annually, during the deicing season, field blanks of all the constituents were collected from the four sampling locations. Field blanks were collected by running reagent water through the full sampling system to simulate sample collection. From 2004 to 2019, 62 field blanks were collected. Of these, 42 samples were analyzed for all three BT isomers, 12 were analyzed for 5-MeBT only, 58 were analyzed for propylene glycol, and 54 were analyzed for potassium. Concentrations of all field blanks were below detection limits.

The laboratory analyzed 36 replicate samples for propylene glycol. Of these, concentrations were below method detection levels for 20 samples and replicates. One sample had a replicate value below the detection level and sample value at a low concentration (5.59 mg/L). Of the remaining samples, the average relative percent difference (calculated by dividing the difference between the sample and replicate by the average of the two and multiplying by 100) between samples and replicates was 7.4%. The laboratory analyzed 36 replicate samples for BTs. Of these, 8 4-MeBT, 9 5-MeBT, and 16 1H-BT samples and replicates were both below detection levels. Four samples had a replicate value that was below the detection level and sample values at low concentrations, ranging from 0.0087 to 0.13 µg/L. Of the remaining samples, the average relative percent difference among all BT samples and replicates was 5.3%. One outlier was excluded from this average, which had relative percent differences for 4-MeBT, 5-MeBT, and 1H-BT of 159%, 156%, and 190%, respectively. The laboratory analyzed 36 replicate samples for potassium. Of these, five samples and replicates were below detection levels. Of the remaining samples, the average relative percent difference between samples and replicates was 2.8%. One outlier was excluded from this average, which had a relative percent difference of 122%. All replicate data are provided in the supplemental information (Table S3).

Matrix spikes were conducted on 34 BT samples. Samples were spiked with 10 µg/L 4-MeBT, 5-MeBT, or 1H-BT. Average matrix spike percent recovery was 110% for 4-MeBT, 92.2% for 5-MeBT, and 104% for 1H-BT. Matrix spikes were conducted on 23 propylene glycol samples, and samples were spiked with 400 mg/L. Average matrix spike recovery was 103%. All matrix spike data are provided in the supporting information (Table S3).

Data analysis

The primary objective of this study was to determine if there have been changes in BT concentrations because of changes in deicer formulations. A direct comparison of concentrations from before to after the deicer formulation changes was not ideal to serve this purpose for a couple of reasons. First, the detection levels of MeBT isomers improved considerably in 2007, complicating the comparison of pre- to post-2007 results, and second, because of the inherent variability of water quality caused by multiple factors that are unrelated to components within the deicer formulations, such as weather patterns during sampled events, precipitation form (e.g., snow, freezing rain), and contributions of deicer to the stream from storage within the watershed (e.g., snowbanks, shallow groundwater system).

To handle the change in detection levels, MeBT results below the detection limit were given a value equal to the detection limit for data analysis purposes except for data from the upstream and receiving stream sites collected before water year 2007. During 2004–2006, most samples from the upstream and receiving stream sites were below the detection limit, and most samples with detections after this period were reported between the two detection levels (40 and 0.25 µg/L).These results were removed from the analysis to avoid bias caused by the higher detection level in the early part of the study. Concentrations for most samples at the two airport outfalls were higher than both detection levels, so values before water year 2007 were included for these sites. Censored data from water year 2007 and later are included in the analysis for all sites.

To account for water quality variability, a regression relation was developed with the BT isomers as response variables and measurements of the freezing point depressant content (propylene glycol and potassium) as predictor variables. This analysis relied on the assumption that the freezing point depressants covary with BT in receiving waters, and a change in this relation over time indicates a change in the amount of BT with respect to the relative amount of deicer presence. Evaluation of the changes in these relations over time was conducted by examining regression equation residual values. A significant change in residuals over time would indicate a change in the relation between response and predictor variables. For example, a reduction in BT presence with relation to the freezing point depressants would be indicated by positive residuals before the deicer formulation change and negative residuals after the change. All data used in regression analysis were log 10-transformed. Data from the upstream reference site were excluded from the regression analysis owing to the absence of a BT source upstream from this site for most sampling periods.

Residual values were generated from the linear regressions and plotted as boxplots across water years. The exact timing of the formulation change could not be determined directly because BT isomers in ADAF formulations were only quantified in the early years and at the end of the study period. To estimate the year of formulation change, boxplots of regression residuals were examined, and a "threshold" water year was identified for each BT isomer as the year at which a change in BT concentrations most likely occurred. Water years with median residual values greater than 0 were characterized as the "pre-period," and water years with median residual values less than 0 were characterized as the "post-period." Samples collected during the threshold year were included in the post-period. Therefore, if 2013 were defined as the threshold year, the pre-period included all samples collected before 1 October 2012, and the post-period included all samples collected after this date.

The Wilcoxon rank-sum test was used to test for significant differences between the residual values generated from the linear regressions for pre-threshold year periods and post-threshold year periods, with significance defined as $p < 0.05$.

RESULTS AND DISCUSSION

Concentrations in deicer and anti-icer formulations

The presence and concentrations of BT isomers have been reduced over time in ADAF, but not in PDM (Table 2). BTs were analyzed during 2019 in three Type I, three Type IV, and two PDM products, and previously for nine Type I and eight Type IV products in 2006 and 2009, and one PDM product in 2009. The 2006 study detected 4-MeBT and 5-MeBT isomers in two of five Type I products and three of four Type IV products, and 1H-BT was not analyzed (Corsi, Geis, Loyo-Rosales, & Rice, 2006). In the 2009 study, the three BT isomers were not detected in Type I products, 4-MeBT and 5-MeBT were present in three of four Type IV products and in the PDM product, and 1H-BT was present in two of four Type IV products (NASEM, 2009). In 2019, only two isomers were detected in two formulations tested: 4-MeBT and 5-MeBT were detected at relatively low concentrations in one Type IV product and at higher concentrations in the liquid potassium acetate PDM. Results from tested formulations in 2019 indicated that BT had been nearly eliminated in ADAF, a substantial reduction from 2006 and 2009 testing, but concentrations of 4-MeBT and 5-MeBT in the liquid potassium acetate pavement deicer analyzed in 2019 were 83% and 37% higher than in the potassium acetate PDM analyzed in 2009, respectively. In 2019, concentrations of 4-MeBT and 5-MeBT in the potassium acetate PDM were 29 and 28 times higher than Type IV formulations, respectively; therefore, concentrations in the PDM formulation compared with the small amounts detected in only one Type IV formulation indicated that PDM is likely the primary source of BT in deicer runoff at MKE and could be a substantial source of BTs to streams receiving airport runoff.

In all Type I and Type IV samples where 4-MeBT was detected, 5-MeBT was detected at a higher concentration; however, the ratio of 4-MeBT/5-MeBT varied by formulation from 0.53 to 0.83 (Table 2). 1H-BT was detected at a similar concentration to 5-MeBT in one Type IV formulation and was the only isomer detected in the second Type IV formulation where it was detected. The concentration of 5-MeBT was also higher than 4-MeBT in PDM with the ratio of 4-MeBT/5-MeBT varying from 0.46 to 0.62. Results indicated that 1H-BT was not often present in deicer products, but when present, it represented a substantial portion of total BT concentrations.

Concentrations of BTs in environmental samples

In all, 264 samples were collected from four airport runoff sampling locations from March 2004 to April 2019. Of these samples, 257 were analyzed for 4-MeBT, 264 were analyzed for 5-MeBT, 244 were analyzed for 1H-BT, 264 were analyzed for propylene glycol, and 259 were analyzed for potassium (Table 3). The primary and secondary outfall sites receive direct runoff from the airport; therefore, these sites had significantly higher concentrations of BTs than the upstream and the receiving stream sites. Concentrations of BTs decreased with dilution from water contributions in the surrounding watershed and potential degradation during transport to the receiving stream 5 km downstream from the airport. Median concentrations at the receiving stream were higher than concentrations at the upstream reference, but lower than the two airport outfalls (Table 3). Concentrations of BTs at the upstream reference site were significantly lower than sites downstream from the airport for all BT isomers.

Temporal reductions in BT

Median 4-MeBT concentrations for the three sites downstream from the airport decreased by approximately 74%, 5-MeBT decreased by 69%, and 1H-BT decreased by 82% from pre-change to post-change periods (Figure 2). Reductions in concentrations of the three BT isomers were statistically significant for all three of the downstream sites ($p < 0.05$). To verify that this reduction was a result of deicer formulation change rather than other potential causes, the relation between deicer freezing point depressant and BT isomer concentrations was explored: Linear regressions were developed with the three BT isomers as response variables and indicators of freezing point depressants as predictor variables (Table 4). Residual values from each regression were examined to determine the year in which a change in the relation between BT concentrations and freezing point depressants occurred, and the likely year in which BT was removed or reduced in ADAF formulations used at MKE. Most regression residual values for 4-MeBT and 5-MeBT were higher than 0 before water year 2013, and lower than 0 in water year 2013 and later (Figure 3). Most regression residual values for 1H-BT were higher than 0

TABLE 2 Concentrations of 4-methyl-1H-benzotriazole (4-MeBT), 5-methyl-1H-benzotriazole (5-MeBT), and 1H-benzotriazole (1H-BT) in commonly used formulations of Type I, Type IV, and pavement deicers

Formulation	Freezing point depressant	BT concentrations (mg/L)			Reference
		4-MeBT	5-MeBT	1H-BT	
Type I					
Product 2019—A	Propylene glycol	<0.35	<0.25	<0.25	Current study
Product 2019—B	Propylene glycol	<0.35	<0.25	<0.25	Current study
Product 2019—C	Propylene glycol	<0.35	<0.25	<0.25	Current study
Product 2009—A	Propylene glycol	ND[a]	ND[a]	ND[a]	NASEM (2009)
Product 2009—B	Ethylene glycol	ND[a]	ND[a]	ND[a]	NASEM (2009)
Product 2009—C	Propylene glycol	ND[a]	ND[a]	ND[a]	NASEM (2009)
Product 2009—E	Propylene glycol	ND[a]	ND[a]	ND[a]	NASEM (2009)
Product 2006—1a	Propylene glycol	204[b]	291[b]	NA	Corsi, Geis, Loyo-Rosales, & Rice et al. (2006)
Product 2006—1b	Propylene glycol	<104[b]	<104[b]	NA	Corsi, Geis, Loyo-Rosales, & Rice (2006)
Product 2006—2	Propylene glycol	<104[b]	<104[b]	NA	Corsi, Geis, Loyo-Rosales, & Rice (2006)
Product 2006—3	Propylene glycol	<104[b]	<104[b]	NA	Corsi, Geis, Loyo-Rosales, & Rice (2006)
Product 2006—4	Ethylene glycol	239[b]	302[b]	NA	Corsi, Geis, Loyo-Rosales, & Rice (2006)
Type IV					
Product 2019—D	Propylene glycol	1.80	3.00	<0.25	Current study
Product 2019—E	Propylene glycol	<0.35	<0.25	<0.25	Current study
Product 2019—F	Propylene glycol	<0.35	<0.25	<0.25	Current study
Product 2009—H	Propylene glycol	144 ± 5.9[a]	237 ± 11.1[a]	219 ± 11.5[a]	NASEM (2009)
Product 2009—I	Ethylene glycol	56.4 ± 2.8[a]	106 ± 5.3[a]	ND[a]	NASEM (2009)
Product 2009—J	Propylene glycol	ND[a]	ND[a]	281 ± 16.5[a]	NASEM (2009)
Product 2009—K	Propylene glycol	428 ± 14.8[a]	732 ± 19.0[a]	ND[a]	NASEM (2009)
Product 2006—1	Propylene glycol	223[b]	267[b]	NA	Corsi, Geis, Loyo-Rosales, & Rice (2006)
Product 2006—2	Propylene glycol	829[b]	1200[b]	NA	Corsi, Geis, Loyo-Rosales, & Rice (2006)
Product 2006—3	Propylene glycol	<106[b]	<106[b]	NA	Corsi, Geis, Loyo-Rosales, & Rice (2006)
Product 2006—4	Ethylene glycol	84.8[b]	106[b]	NA	Corsi, Geis, Loyo-Rosales, & Rice (2006)
Pavement					
Product 2019—G	Potassium acetate	53.0	85.0 [c]	<0.25	Current study
Product 2019—H[d]	Sodium acetate	ND	ND	ND	Current study
Product 2009—L	Potassium acetate	28.9 ± 1.4[a]	62.2 ± 2.8[a]	ND[a]	NASEM (2009)

Abbreviations: NA, not analyzed; ND, not detected.
[a]Mean value ± standard deviation (SD); $n = 3$.
[b]Concentrations calculated from mass using specific gravity of 1.04 for Type I formulations and 1.06 for Type IV formulations (Corsi et al., 2012).
[c]Result approximate, above upper calibration range.
[d]Product 2019—H was a granular solid deicer whereas all others were liquid.

before water year 2010, and lower than 0 in water year 2010 and later (Figure 3). Therefore, water years 2013 (4-MeBT and 5-MeBT) and 2010 (1H-BT) were defined as the years at which a change in the relations between BT concentrations and freezing point depressant concentrations occurred

(Table 4). Residuals for all three BT isomers were significantly lower in the post-change periods ($p < 0.01$; Table 4). These differences in regression residuals signified a change in the fundamental relation between freezing point depressants and BT isomers, indicating that the reduction in

TABLE 3 Summary statistics of airport deicer-related water quality constituents from samples collected upstream from the Milwaukee Mitchell International Airport, at airport outfalls, and from the receiving stream 5 km downstream from the airport, 2004–2019

Parameter	Site	Median	Mean	Maximum	*n*
1H-BT (µg/L)	Upstream reference	0.25	0.295	0.93	64
	Primary outfall	0.695	2.25	18	66
	Secondary outfall	1.3	12.8	150	50
	Receiving stream	0.4	0.71	3.2	64
4-MeBT (µg/L)	Upstream reference	1.3	1.86	8.9	63
	Primary outfall	39.5	85.7	740	74
	Secondary outfall	33.5	193	4600	58
	Receiving stream	6.55	8.86	53	62
5-MeBT (µg/L)	Upstream reference	1.1	1.92	15	64
	Primary outfall	42	103	1100	77
	Secondary outfall	46	211	6600	59
	Receiving stream	6.75	10.8	79	64
Potassium (mg/L)	Upstream reference	5.56	6.12	21.1	63
	Primary outfall	88.4	122	1570	75
	Secondary outfall	58	165	2290	58
	Receiving stream	19.1	22.3	108	63
Propylene glycol (mg/L)	Upstream reference	20	38.7	340	64
	Primary outfall	340	773	6500	77
	Secondary outfall	930	3530	70 000	59
	Receiving stream	40	92.7	770	64

BT isomer concentrations was likely to have been caused by the reduction in BT concentration in deicer formulations (Table 2). Because the number of deicer manufacturers is limited, the formulations used in the current study represent a substantial cross section of available deicers in countries with climates that require deicing (Mericas et al., 2020). As such, demonstration of significant reductions in BTs in runoff from MKE is a likely indication of similar changes at airports in the United States and other countries that use these deicers.

Information on the content of BTs in airport runoff since the change in deicer formulations is currently lacking; however, several international studies before the formulation change measured BTs in rivers that were likely influenced by airport runoff. In one previous study, concentrations of 1H-BT in surface and groundwater samples collected in the area of the Fornebu Oslo airport in Norway were measured between 1.5 and 33 µg/L; 4-MeBT and 5-MeBT were detected only in trace amounts (Breedveld et al., 2002). Concentrations of 1H-BT in studies from rivers with airport influence in Europe (Giger et al., 2006; Kiss & Fries, 2009, 2012) and China (Heeb et al., 2012) varied from 0.04 to 5.4 µg/L, which were similar to concentrations in the receiving stream site from the current study but lower than

concentrations in the primary and secondary outfalls that received direct inputs from the airport. Concentrations of 4-MeBT and 5-MeBT in these studies (where measured), however, tended to be lower than the concentrations measured in the current study, varying from 0.025 to 4.3 µg/L (Giger et al., 2006; Kiss & Fries, 2009, 2012). Concentrations of BTs in surface water without airport influence are generally lower than those in airport runoff; in fact, one review of BT occurrence in the environment (Shi et al., 2019) found a maximum 1H-BT concentration of 8.5 µg/L, 5-MeBT concentration of 7.2 µg/L (Molins-Delgado et al., 2017), and 4-MeBT concentration of 1.6 µg/L (Jover et al., 2009) in Spanish rivers without known airport influence. In the United States, a 1999–2000 survey of various organic wastewater contaminants in 139 streams, not necessarily influenced by airport runoff, across 30 states found a maximum 5-MeBT concentration of only 2.4 µg/L (Kolpin et al., 2002), which is similar to concentrations found at the upstream reference site in this study, but generally much lower than concentrations found at airport-influenced sites. After the deicer formulation change identified in this study, one 2014–2015 Canadian study measured BTs in rivers influenced by the Pearson Airport, and the company that supplied ADAF to the airport did not use BTs in their formulations at the time
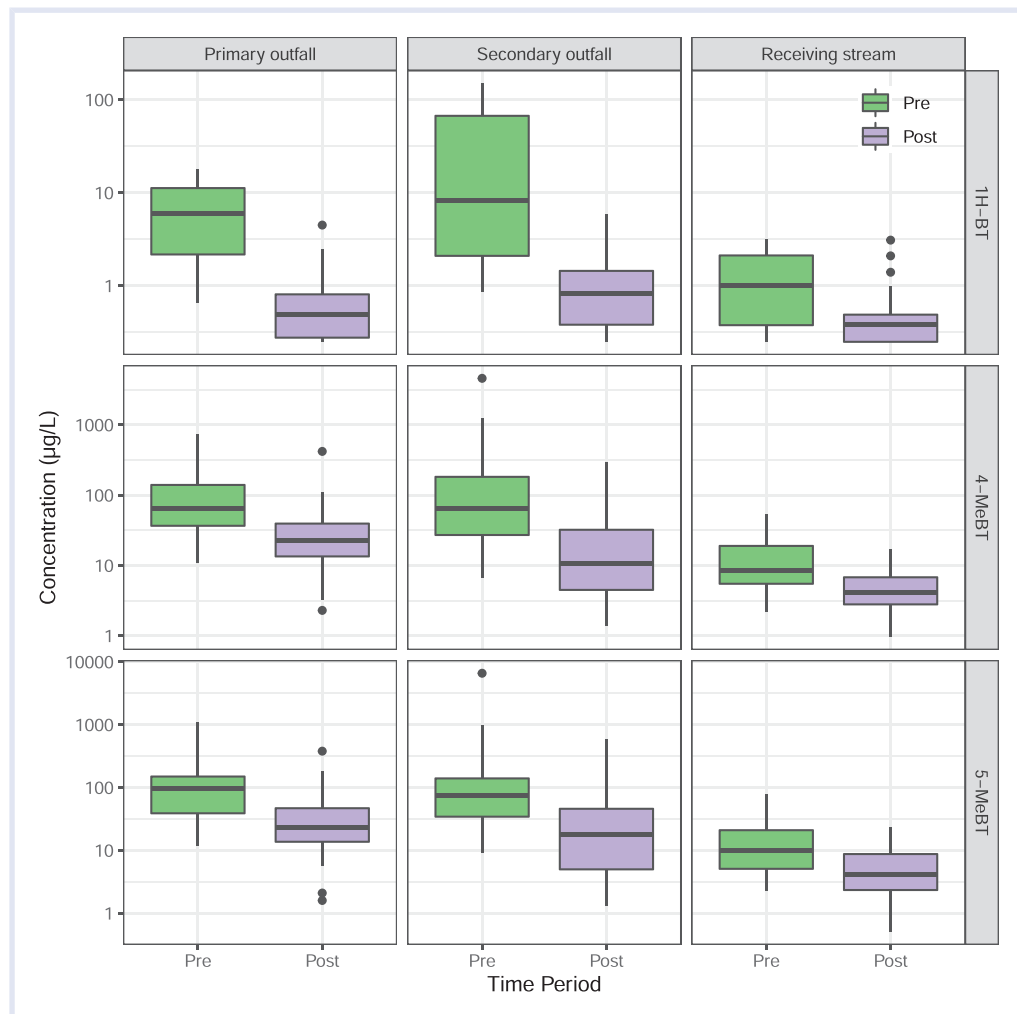
FIGURE 2 Concentrations of benzotriazole (BT) isomers at two airport outfalls and in the stream receiving runoff from Milwaukee Mitchell International Airport, 2004–2019. Data collected before October 2009 for 1H-benzotriazole (1H-BT) and data collected before October, 2012 for 4-methyl-1H-benzotriazole (4-MeBT) and 5-methyl-1H-benzotriazole (5-MeBT) were considered to be the period before deicer formulations changed (Pre) and after which BT content in deicers were reduced (Post). Boxes display the 25th percentile, median, and 75th percentile, whiskers display the minimum and maximum values, and points display outliers

TABLE 4 Results from linear regression models, median concentrations of BT pre- and post-water quality change, and significance level from Wilcoxon rank-sum tests to compare regression residuals from pre- and post- water quality change period in stream sample results downstream from Milwaukee Mitchell International Airport, Milwaukee, Wisconsin

Response variable	Predictor variables	Coefficient	Adjusted R^2	Pre-post-period threshold year	Median concentrations (µg/L)		Residuals
					Pre-period	Post-period	Significance level
4-MeBT	Propylene glycol	0.26	0.62	2013	39	10	<0.01
	Potassium	0.75					
5-MeBT	Propylene glycol	0.29	0.65	2013	43.5	13.5	<0.01
	Potassium	0.78					
1H-BT	Propylene glycol	0.36	0.26	2010	2.5	0.44	<0.01
	Potassium	0.12					

Note: All variables in the regressions were log-10 transformed.
Abbreviations: 4-MeBT, 4-methyl-1H-benzotriazole; 5-MeBT, 5-methyl-1H-benzotriazole; 1H-BT, 1H-benzotriazole.
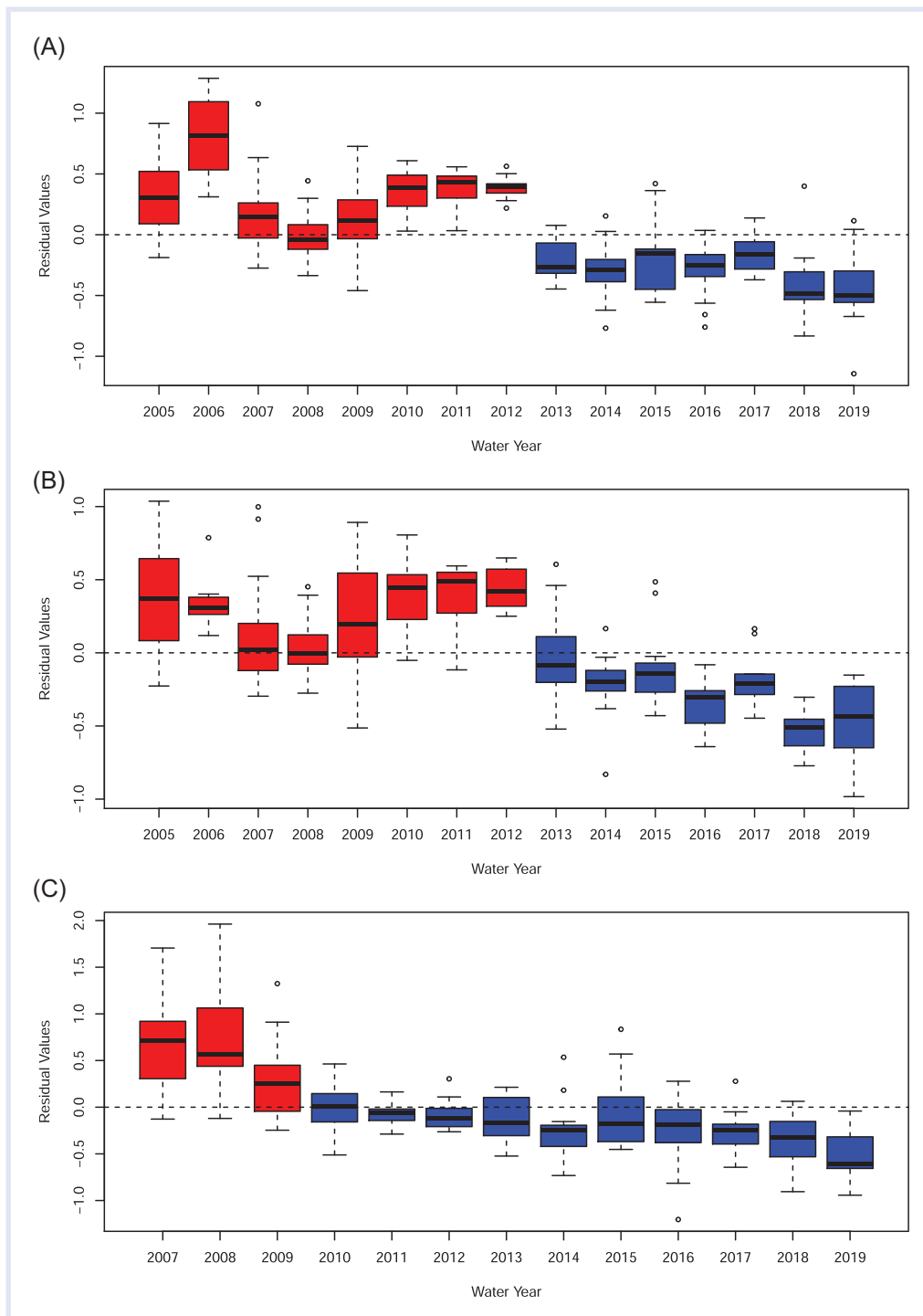
FIGURE 3 Regression residual values for (A) 4-methyl-1H-benzotriazole (4-MeBT), (B) 5-methyl-1H-benzotriazole (5-MeBT), and (C) 1H-benzotriazole (1H-BT) by water year. Boxplots in red are years before the water quality change and boxplots in blue are years after the water quality change. Boxes display the 25th percentile, median, and 75th percentile, whiskers display the minimum and maximum values, and points display outliers

of the study (Parajulee et al., 2017). 1H-BT concentrations varied from 0.00091 to 2.39 µg/L, which was similar to concentrations measured in this study after the formulation change. However, concentrations of 4-MeBT varied from 0.00144 to 1.99 µg/L, and 5-MeBT varied from not detected to 0.45 µg/L, which were lower than concentrations

measured in this study even after the formulation change. Several BT sources other than airport deicers have been identified, including wastewater inputs, often reported to be present at concentrations up to tens of micrograms per liter (Loos et al., 2013; Molins-Delgado et al., 2015, 2017; Voutsa et al., 2006) and dishwashing detergents reported to be less

than 10 µg/L (Alotaibi et al., 2015). These sources are likely to be diluted by receiving streams resulting in concentrations similar to or lower than concentrations reported in the current study after the deicer formulation change.

Implications for aquatic life

Previous studies have observed that BTs contributed to the aquatic toxicity of deicers, particularly for microorganisms tested with the Microtox assay (Cancilla et al., 1997; Cornell et al., 2000; NASEM, 2009). Ecologically significant concentrations have been observed in surface water and groundwater receiving airport runoff (Cancilla, 1998; Cancilla et al., 2003; Corsi, Geis, Loyo-Rosales, Rice, Sheesley et al., 2006). In vivo toxicity testing has been conducted in previous studies on a variety of organisms (Cancilla et al., 2003; Corsi, Geis, Loyo-Rosales, & Rice, 2006; Li, 2013; Pillard et al., 2001; Seeland et al., 2012). Resulting effect concentrations indicated that organisms were typically more sensitive to 5-MeBT than 4-MeBT and 1H-BT (Table S2).

Five environmental samples from the primary outfall and five samples from the secondary outfall had concentrations that exceeded the 10% effect concentration (EC_{10}) for the *Daphnia galeata* 21-day reproduction test for 5-MeBT (400 µg/L; Seeland et al., 2012). One sample, with a 5-MeBT concentration of 6.6 mg/L in January 2005 at the secondary outfall, exceeded 12 of the effect concentrations in Table S2 for acute toxicity (Microtox assays) and chronic toxicity (measures of reproduction and population in *D. galeata*, *Daphnia magna*, *Lemna minor*, and *Desmodesmus subspicatus*; Cancilla et al., 2003; Corsi, Geis, Loyo-Rosales, & Rice, 2006; Seeland et al., 2012). The sum of 4-MeBT and 5-MeBT concentrations in the same sample was 11.2 mg/L, which exceeded three of the effect concentrations in Table S2 for acute toxicity (Microtox assays) and chronic toxicity (measures of reproduction in *Ceriodaphnia dubia*; Corsi, Geis, Loyo-Rosales, & Rice, 2006; Pillard et al., 2001). Of these exceedances, all but one sample was collected before 2013, when a significant reduction in BT concentrations was observed, likely owing to the removal of BTs from Type I and Type IV aircraft deicing and anti-icing fluids. Samples collected from 2014 through 2019 were not found to exceed endpoint concentrations in Table S2.

Conservative water quality benchmarks have commonly been computed as 10% of the lowest bioassay endpoint for development of water quality benchmarks (an "application factor" of 0.1; Hull et al., 2015). Using this technique, concentrations from 75 samples exceeded benchmarks for BT isomers (benchmark values in brackets): 75 for 5-MeBT (40 µg/L), 1 for 4-MeBT (2,100 µg/L), 2 for 1H-BT (97 µg/L), and 13 for the sum of 4- MeBT and 5-MeBT (570 µg/L). Of these exceedances, 73 were from samples collected at the two outfall sites and two from the receiving stream site. Forty-one percent of samples collected during the prechange period (2013 water year) and 15% during the postchange period exceeded benchmark values. Though exceedance of these benchmark values has periodically occurred since 2013, the frequency has decreased over time. Exceedance of benchmark values since 2013 is likely caused by the presence of BTs in current-use PDM.

CONCLUSIONS

Analysis of BT isomers in ADAFs and airfield-PDM formulations from 2019 indicated that BT had been removed or substantially reduced since analysis in 2006 and 2009 in ADAF, but BT concentrations in PDM formulations had not been reduced. Monitoring of BTs in airport runoff from 2004 through 2019 provided an evaluation of the change in BT concentrations in runoff samples over time resulting from the reduction or removal of BTs in ADAF formulations. BT concentrations and regression analysis indicated a decrease in BT concentrations in airport runoff in 2013 for 4-MeBT and 5-MeBT, and 2010 for 1H-BT, indicating that BTs were removed or significantly reduced from ADAF formulations in these years. The frequency of exceedance of water quality benchmarks has been reduced since 2013, indicating that the potential hazard level for aquatic organisms has been reduced as a result of the removal of BTs from ADAFs. The presence of BT in potassium acetate PDM formulations indicates that a continued aquatic life hazard from these compounds may exist in water bodies receiving airport deicer runoff.

Because the deicer formulations investigated in this study are used throughout the United States and other countries, these results have broad implications with regards to BTs in airport runoff. Although airports do not typically include deicer additives in stormwater permit monitoring requirements, it is not uncommon for aquatic toxicity criteria to be included. The MKE case study demonstrated that the reduction or removal of harmful contaminants in deicer formulations can reduce concentrations and associated hazards to aquatic life in receiving streams, thereby providing a greater likelihood of meeting aquatic toxicity requirements in stormwater permits at airports throughout the United States and other countries.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest.

DISCLAIMER

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the US Government.

DATA AVAILABILITY STATEMENT

Data used in this study are available in the Supplemental Data files and the US Geological Survey National Water Information System (https://doi.org/10.5066/F7P55KJN). Requests for data may be sent to Steven Corsi (srcorsi@usgs.gov).

SUPPORTING INFORMATION

TABLE S1. Table of propylene glycol, potassium, 4-methyl-1H-benzotriazole (4-MeBT), 5-methyl-1H-benzotriazole (5-MeBT), and 1H-methyl-1H-benzotriazole (1H-BT) concentrations from four sampling sites near the Milwaukee Mitchell International Airport (MKE) from 2004–2019 (XLSX).

TABLE S2. Table summary of toxicity data for three benzotriazole (BT) isomers and a 4-methyl-1H-benzotriazole, 5-methyl-1H-benzotriazole mixture (PDF).

TABLE S3. Table of laboratory replicate and matrix spike data for propylene glycol, potassium, 4-methyl-1H-benzotriazole (4-MeBT), 5-methyl-1H-benzotriazole (5-MeBT), and 1H-methyl-1H-benzotriazole (1H-BT). Matrix spike concentrations were 400 mg/L for propylene glycol and 10 µg/L for benzotriazoles.

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