**Title**

**Abstract**

**Introduction**

The release of aircraft deicers and anti-icers (ADAF) and chemical pavement deicing and anti-icing material (PDM) to the environment has the potential to cause damaging effects on aquatic ecosystems including aquatic toxicity1–3, elevated biochemical oxygen demand (BOD) and chemical oxygen demand (COD), which results in depressed dissolved oxygen levels4–7, and possible endocrine disruption due to the degradation products of ADAF additives 8. Nationally, the U.S. EPA estimates that U.S. commercial airports use on average 25 million gallons per year in ADAF and roughly 35,500 tons per year of PDM, while on average U.S. commercial airports discharge approximately 21 million gallons of ADAF (50% concentration) annually to surface waters 9. Glycols contained in ADAF and PDM have large amounts of BOD and COD. Concentrations of these constituents in airport effluents vary dramatically depending on climate, hydrologic and ADAF and PDM management approaches. Previous field studies from 2006 – 2015 at General Mitchell International Airport (GMIA) in Milwaukee, WI have concentrations of propylene glycol, 5-day BOD (BOD5) and COD in airport effluent as high as 6500 mg/l, 3100 mg/l and 15,300 mg/l, respectively.

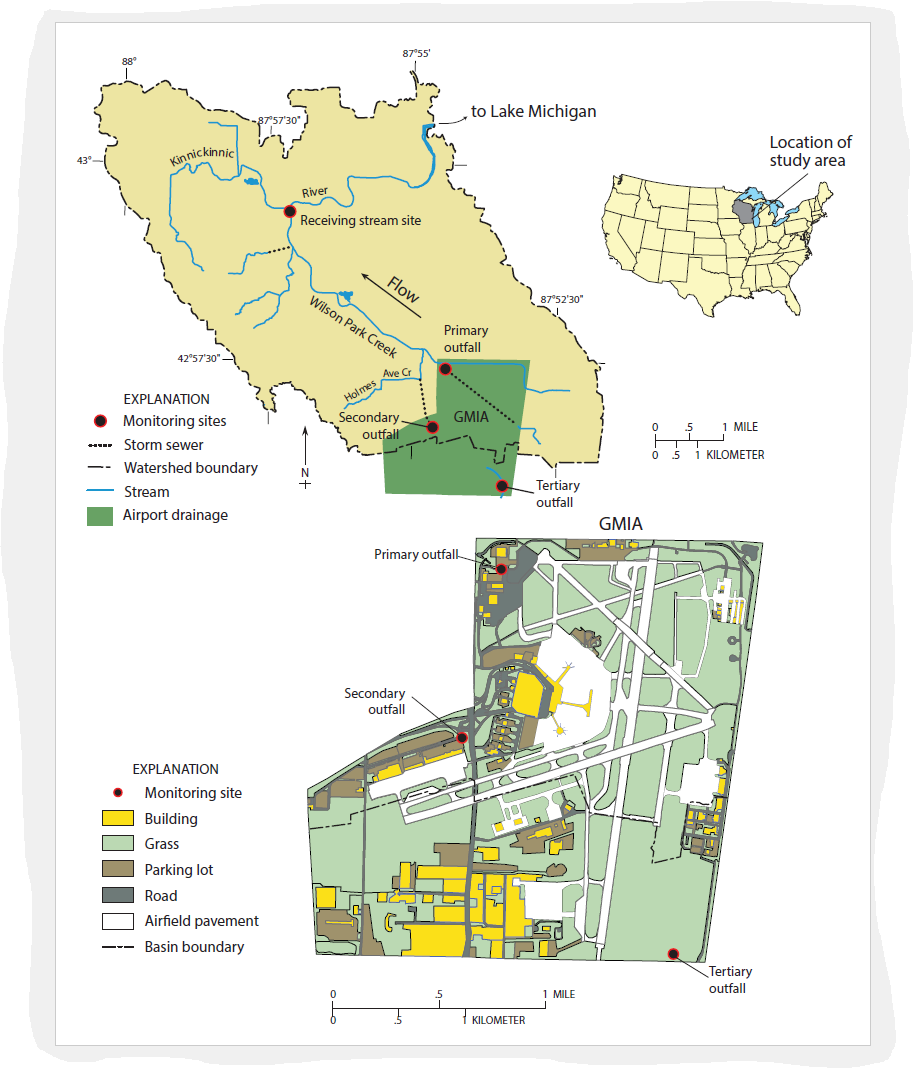
During periods of freezing precipitation, airports must clear snow and ice from aircraft, runways, taxiways and other paved surfaces to maintain daily operations and schedules. Mechanical snow removal by snow plows and rotary snow brooms are used to remove loose snow and ice from paved surfaces, but when physical removal is not sufficient, the use of liquid and solid PDM becomes necessary. Direct application of liquid PDM helps to melt existing snow and ice and reduce adhesion to pavement, which enhances the effectiveness of physical removal systems. In addition, application of liquid PDM to pavement surfaces in advance of freezing precipitation events prevents adhesion to pavement, which facilitates physical removal. Solid PDM is applied directly to penetrate existing ice, followed by liquid PDM application to reduce adhesion to paved surfaces. In addition, ice and packed snow warrant application of a mixture of sand and solid PDM to enhance traction. Application rates of these chemical deicers vary by airport and environmental conditions, however, the greatest application rates are recommended at intersections and high traffic areas. Similarly, ADAF are applied to the wings and fuselage of aircraft to remove and prevent snow and ice buildup from aircraft surfaces that would otherwise delay and prevent safe air travel. Application rates of ADAF products vary, however airports located in colder climates use ADAF practically every day of the winter season to some degree. Airports in warmer latitudes use them less frequently, but freezing precipitation warrants the use of ADAF nearly every year even at these warmer climate airports such as those in the southern United States 10,11.

PDM and ADAF consist primarily of freezing point depressants (FPD), water, and lesser concentrations of various additives such as corrosion inhibitors, surfactants, dyes, flame retardants, anticaking chemicals and pH buffers. Current FPDs used in liquid PDM include potassium acetate-, potassium formate-, propylene glycol (PG)- and ethylene glycol (EG)-based fluids. FPDs used in solid PDM include sodium acetate and sodium formate. Airside urea PDM formulations are available in solid (granular) and in liquid form mixed with ethylene or propylene glycol. In addition to chemical PDM, sand is used for added surface friction. Current FPDs used in ADAF include PG, EG or diethylene glycol. Fluid designations of ADAF are based on aerospace material specifications published by the Society of Automotive Engineers (SAE). Type I fluids are deicers used for removing ice, frost and snow from aircraft surfaces. Type I fluids are diluted with as much as 80% water and heated to between 150 and 180 °C before application. Type II and IV fluids are more viscous anti-icers applied at full strength at ambient temperatures to prevent the formation of ice and snow on aircraft. Type IV anti-icers are more frequently used by major airlines, while Type II anti-icers are mostly used by smaller airlines due to financial concerns 6,9–11.

The fate and transport of PDM and ADAF varies due to many factors such as the individual airport, deicer collection facilities implementation, management of deicer contaminated stormwater, the nature and timing of precipitation, wind drift, plowing to snowbanks, melting of snowbanks, overspray during aircraft application, dripping from aircraft during taxi and holdover activity, takeoff sheer, seepage through pavement joints and into pervious areas, tracking by aircraft and ground-support vehicles, drainage to surface-and/or groundwater systems and eventual degradation. Some applied PDM that is not collected through runoff management degrades near the point of application 12, while it is presumed the remainder is discharged to soil, ground- and surface water systems near airports. However, PDM and ADAF fate is different due to the nature of how and where they are used. PDM tends to be applied across a large area throughout airports, and as a result containment of PDM into a deicer management system is difficult and costly. For this reason, many deicer-runoff-management systems in airports focus on ADAF application areas. Many airports have implemented some form of ADAF management to reduce runoff to receiving waters. Typical management practices include deicing pads, glycol recovery vehicles, storm sewer balloons and snow containment systems 13. Some airports reduce ADAF usage at the source by variably mixing water with ADAF 13, mixing with forced hot air during application, or using non-glycol alternatives such as infrared technology to remove ice and snow from aircraft 14.

The primary objective of the ongoing research at GMIA is to investigate and monitor the effects ADAF and PDM have on receiving waters. Research began in 1996 and has focused on BOD and dissolved oxygen in airport outfalls and receiving streams, aquatic toxicity of ADAF and PDM and runoff containing the two, occurrence and effects of ADAF and PDM additives, and the effects of ADAF and PDM in snowbanks and snowmelt. Continuous monitoring of outfalls receiving ADAF and PDM during periods of freezing precipitation is ongoing and costly to perform. The objective of this paper is to explore and present alternative techniques to predict ADAF and PDM presence and magnitude in outfalls draining GMIA.

**Methods**



**Figure 1.** Location of field study area and monitoring locations

*Site Description*

Surface water samples were collected at four locations near General Mitchell International Airport (GMIA) over two freezing precipitation seasons (November 1 – May 1) from December 2013 – May 2015. Of the four sampling locations, three were airport outfalls (a primary, secondary and tertiary), and the fourth was a receiving stream (Fig. 1). In total, ### precipitation runoff event samples were collected from the four sampling locations with some sites having greater collection frequencies than others (Table 1). Two airport outfall locations were sampled and drain to Wilson Park Creek (WPC). The primary outfall location includes flow from a 2.31 km2 upstream headwater region of WPC in addition to flow from the storm sewers draining the terminal area as well as some taxiways and runways. The secondary outfall drains a small area of the airport where most air cargo activities take place. The secondary outfall discharges into Holmes Ave. Creek, a small tributary of WPC, which at the confluence is ~ 0.8 km downstream from the primary outfall. Drainage area of the primary outfall is 5.83 km2 (3.52 km2 representing the airport facility) while the drainage area of the secondary outfall is 0.08 km2. The receiving stream is situated 5.54 km downstream from the airport. This site was chosen in order to characterize water quality effects on the receiving stream. The stream between the airport and the receiving stream location alternates between concrete-lined and earthen channel bottom. The drainage area of the receiving stream location (i.e. WPC) is 14 km2. Immediately beyond the receiving stream location, the stream confluences with the Kinnickinnic River, which flows for 4.33 km to the Kinnickinnic River estuary and eventually into Milwaukee Harbor. The fourth location, tertiary outfall, flows south out of GMIA and was used to collect grab samples only. As GMIA has grown over the years, airport operations (i.e. runways, taxiways, etc) have moved into the tertiary outfall watershed and samples were collected to determine the influence of aircraft deicer materials leaving airport property via this outfall. Samples collected from the tertiary outfall were grabbed at roughly the same location; where the stream intersects with W. College Ave, prior to any confluence with additional water sources. The tertiary outfall eventually drains to Oak Creek which discharges directly into Lake Michigan.

*Surface-Water Sampling*

Flow-weighted water quality samples were collected using refrigerated automatic samplers with Teflon-lined polyethylene sample tubing and 10L glass collection bottles (model 3700R, Isco Industries, Lincoln, NE). In addition to the 10L glass collection bottle above, the primary outfall location collected flow-weighted water quality samples into 350 ml glass collection bottles (model 3700R, Isco Industries, Lincoln, NE). Additional specific details regarding the sampling protocol have been previously described 3. Various bottle collection types and numbers of samples were collected from the five monitoring locations (Table 2). After each runoff period, or sampling period, samples were collected, iced and then transported to the Middleton, WI U.S. Geological Survey field office for processing. Samples were subsequently split for separate chemical and optical analysis, filtered (if required), preserved (if required), iced and delivered to the laboratory within 24 h. Constituents reported in this paper include propylene glycol, ethylene glycol, acetate, chemical oxygen demand (COD), absorbance and dissolved organic carbon (DOC). Field blanks were collected at each of the five locations and samples were submitted for all constituents listed above.

*Chemical Analysis*

All chemical analyses, except DOC and absorbance, were conducted at the Wisconsin State Laboratory of Hygiene (WSLH). DOC and absorbance samples were analyzed at the US Geological Survey, Wisconsin Water Science Center. Acetate was analyzed using methods as defined in the manual for the DIONEX AS15 separator column (DIONEX, Sunnyvale, CA). Additional details regarding DIONEX instrument conditions was previously described 10. Reporting levels were determined as the concentrations below which spike recoveries exceeded 25% uncertainty (5 mg/L for acetate). Samples for acetate were filtered (PALL, Acrodisc ® 0.2 µm nylon membrane, 25 mm capsule syringe filter) into one 40 ml plastic bottle. Samples collected for glycol were filtered (Whatman, 0.2 µm CA filter media, 25mm polypropylene capsule syringe filter) into two individual 40 ml plastic bottles. Raw surface water for COD samples was preserved with 1.0 ml of a 1 to 3 sulfuric acid solution in a 250 ml plastic bottle prior to delivery to WSLH. Methods for the analysis of propylene glycol and COD have been previously published 15,16.

*Dissolved Organic Carbon (DOC) and Optical Analysis*

Environmental samples for DOC and optical analyses were filtered (Whatman® glass microfiber syringe filters, pore size 0.45 µM) into two pre-combusted 40 ml amber glass vials. Deicer and anti-icer products (Table ##) were unfiltered and analyzed for DOC and optical analysis. For both DOC and optical analysis of the deicer and anti-icer products, serial dilutions were performed to get the samples in range for both analytical instruments. Environmental samples were diluted to get samples in range for both analytical instruments when needed. Both sample vials were stored in the dark at 4 °C until sample analysis. All samples for optical analysis were analyzed within 5 days of collection, and DOC samples were processed within 14 days of collection.

DOC samples were analyzed using a Shimadzu TOC-VCSH analyzer, which employs a catalyst-aided platinum 680 °C combustion technique, coupled with the Shimadzu ASI-V Auto sampler. The non-purgeable organic carbon (NPOC) analysis method was employed, in which samples were sparged with 2 M HCL to remove all inorganic carbon prior to combustion. The resultant NPOC concentrations, given in units of mg/L, were calculated as a mean of three valid measurements with a maximum standard deviation of 0.1 mg/L. Based on long-term monitoring of blank concentrations from ultra-pure 18.2 megohm water, method detection limit (MDL) for the Shimadzu system is 0.2 mg/L.

A fluorescence excitation-emission matrix (EEM) and absorbance scan measurements were performed using a Jobin Yvon Aqualog benchtop Spectrofluorometer. EEMs were generated using excitation (ex) wavelengths of 240 – 800 nm at intervals of 3 nm and emission (em) wavelengths of 247 – 827 nm at intervals of 2.33 nm with an integration time of 1 s and a CCD gain set at medium. Absorbance and fluorescence analysis were performed in a 1-cm path-length quartz cuvette. Samples were diluted with ultra-pure 18.2 megohm water and re-run if UV-Visible absorption data at 254 nm (A254) exceeded 0.3 absorbance units to limit inner filter effect problems 17. Spectra were corrected for inner filtering effects, Rayleigh 1st and 2nd order masking using automated algorithms supplied with the Aqualog software. Fluorescence intensity was normalized to a Starna (Starna Cells, RM-QS00) certified quinine sulfate standard. All samples were blank corrected against a Starna (Starna Cells, 3Q-10) certified Raman calibration standard.