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# THE ACUTE WHOLE EFFLUENT TOXICITY OF STORM WATER FROM AN INTERNATIONAL AIRPORT

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**Abstract**—In October 1990, the U.S. Environmental Protection Agency promulgated application requirements with deadlines for storm-water dischargers associated with industrial activity and certain municipal systems. Major airports have a number of hydrocarbon-based contaminants that could appear in storm-water runoff. In addition, ethylene, diethylene, and propylene glycol deicing and anti-icing mixtures are used during freezing and near-freezing weather. The objective of this study was to characterize the potential acute impact on aquatic life from industrial storm-water discharges from an international airport. Samples from winter storm events caused acute toxicity to both the fathead minnow (*Pimephales promelas*) and the daphnid (*Daphnia magna*), with LC50 values for both species as low as 1.0 to 2.0% effluent. The toxicity of the samples was due to the various glycol-based deicer/anti-icer mixtures used during these events. High oxygen demands and elevated total nitrogen levels are other potential problems during anti-icing/deicing activities. Samples from rain events during the nonwinter months at the airport did not cause acute toxicity unless associated with fuel spills. As a result of this study, a new discharge permit has been issued for this airport, requiring the implementation of plans for the collection and recycling and/or disposal of the deicer/anti-icer mixtures.

**Keywords**—Storm water   Acute toxicity   Deicing mixtures   Freshwater   Airport

## INTRODUCTION

The Maryland Department of the Environment (MDE) has an aggressive program for whole effluent toxicity (WET) under its National Pollutant Discharge Elimination System (NPDES) permit program. In 1987, MDE began a biomonitoring campaign of all industrial and major municipal dischargers that has, to date, accounted for more than 95% of the industrial dischargers. The MDE requires a toxicity reduction evaluation (TRE) for all dischargers that have confirmed acute toxicity. Also, the MDE requires biomonitoring for chronic toxicity where appropriate.

In October 1990, the U.S. Environmental Protection Agency (EPA) promulgated regulations addressing storm-water discharges. Specifically, the EPA promulgated application requirements with deadlines for storm-water dischargers associated with industrial activity and for storm water from certain municipal systems. Prior to these regulations, storm water had generally been unregulated. Thus, very little information is available concerning the WET characterization of storm water.

Major airports have a number of possible contaminants that could appear in storm-water runoff. The majority of these are hydrocarbon based (fuel, oil, rubber products). In addition to these classes of more common contaminants are the ethylene, diethylene, and propylene glycol deicing and anti-icing mixtures used during freezing weather and snowstorms. Two types of mixtures are used by Baltimore-Washington International Airport (BWI). Type I deicing mixtures are unthickened, contain a minimum of 80% glycols by weight, and are primarily ethylene glycol based. Type II anti-icing mixtures contain at least 50% glycols by weight and are propylene glycol based. The Type II mixtures contain thickening agents that enable the solutions to stick to the treated surfaces and therefore inhibit ice formation while the aircraft is stationary. Both Type I and II mixtures contain other possible toxicants including the animal carcinogen 1,4-dioxane, which occurs in trace amounts in technical-grade ethylene glycol.

Some laboratory data exist on the toxicity of these various components of airport runoff, but there exist little data on the possible WET of storm water from such a facility. MacDonald et al. [1], Hartwell et al. [2], and Pillard [3] reviewed the literature on glycol toxicity and reported LC50 values ranging from 7,417 mg/L for 1,3-propylene glycol and the daphnid (*Daphnia magna*) to 75,200 mg/L for diethylene glycol and the fathead minnow (*Pimephales promelas*). Ethylene glycol is acutely toxic to the fathead minnow and daphnid in the 40,000 to 50,000 mg/L range. In laboratory studies involving Type I and II mixtures, both Hartwell et al. [2] and Pillard [3] found these mixtures to be more acutely and chronically toxic than pure ethylene and propylene glycol. In addition, propylene glycol Type II mixtures were more toxic than ethylene glycol Type I mixtures.

The objective of this study was to begin to characterize the potential acute impact on aquatic life from industrial storm-water discharges from an international airport. The MDE contracted the Bioassay Laboratory at the University

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of Maryland's Wye Research and Education Center (WREC) to design and implement this storm-water toxicity investigation. The study was conducted in conjunction with an ongoing environmental monitoring program being conducted for BWI Airport by Maryland Environmental Services (MES), of Annapolis, Maryland.

## MATERIALS AND METHODS

### *Project description*

This study was designed to investigate the acute toxicity of storm water from the Baltimore–Washington International Airport. This site has a U.S. Weather Service climatological monitoring station that facilitates the recording of storm events, including their duration and intensity. The facility also has existing storm-water collection, flow analysis, and chemical analysis programs that complement the current project. Toxicity testing was conducted at two storm-water discharge points receiving discharges from aircraft and/or runway deicing/anti-icing activities during winter storm events. The testing program was originally designed for quarterly acute toxicity testing for 1 year. However, because there were two snow/ice events during the first quarter of the project, storm water from these events was sampled to better characterize the discharges associated with deicing/anti-icing activities. Information on the sample sites and events is summarized in Table 1.

### *Sample sites*

Site No. 1 (Kitten Branch) is a storm-water discharge pipe that handles runoff from the main terminal area, including the primary deicing/anti-icing area (p-patch). This pipe discharges directly to Kitten Branch, which runs through the airport property and flows to Stoney Run and then to the Patapsco River and the Chesapeake Bay. The sample location was prior to discharge to Kitten Branch. Site No. 4 (Muddy Bridge Branch) is the outfall from a storm-water collection pond that receives storm water and deicing/anti-icing mixture from the commuter flight area. Muddy Bridge Branch discharges to Saw Mill Creek and eventually to the Chesapeake Bay through Curtis Bay. Samples were collected prior to discharge into Muddy Bridge Branch.

These two sites represent the majority of point-source storm-water drainage from the airport property. Additionally, these sites drain the areas where all of the deicing/anti-icing activities occur. The drainage area for both sites is mostly paved surfaces.

### *Sample collection*

Automated samplers (ISCO©, Lincoln, NE) were used to sample throughout storm events. The samplers were programmed to take 500-ml samples every 15 min for 12 h. No individual storm event during the study lasted longer than 12 h. Samples were stored in 1-L containers in the sampler. For events during deicing/anti-icing operations, samples were visually checked for pink color and analyzed with a refractometer (Reichert refractometer, Cambridge Instruments, Buffalo, NY) after the event, and the most concentrated samples were composited for a worst-case scenario. The composite samples were split for toxicity testing and chemical analysis. In addition, at Site No. 1, a separate sampler collected a composite sample (500 ml every 15 min) for the entire storm event for toxicity testing. Thus, toxicity information was obtained for both a worst-case and average exposure for each storm event.

For events not associated with deicing/anti-icing operations (spring, summer, and fall quarters), a different sampling regime was used. Where possible, a composite was made of the first few samples during the event to catch the initial runoff at both sites. In addition, at Site No. 1, a separate sampler was used to collect a composite for the entire event, if possible. Thus, samples were to be collected for a worst-case and average exposure for each of these events. As discussed below, one event was too short to collect a 12-h composite, so only a worst-case sample was collected.

At the end of the sampling period, samples were transported to the WREC toxicology laboratory. Samples were not refrigerated during collection. Toxicity tests began within 36 h of collection of the samples. If the tests began within 2 to 3 h after collection, samples were not refrigerated during transportation. If the tests were delayed, the samples were refrigerated during transportation and holding. The sample to be used for the 24-h renewals was refrigerated.

### *Test organisms*

Each sample was tested with two species, the daphnid (*D. magna*) and the fathead minnow (*P. promelas*). Organisms were obtained from the existing cultures maintained at the

Table 1. Site and event descriptions for BWI airport storm-water study

| Site No. | Site description | Event No. (date) | Event type | Test type (date) |
|---|---|---|---|---|
| 1 | Runoff from main terminal area prior to discharge to Kitten Branch | 1 (2/12/93) | deicing/anti-icing[a] | Peak and Composite (2/13/93) |
| | | 2 (2/26/93) | anti-icing/deicing[b] | Peak and Composite (2/27/93) |
| | | 3 (10/20/93) | rain | Peak and Composite (10/21/93) |
| | | 4 (10/26/93) | rain | Peak (10/27/93) |
| 2 | Runoff from storm-water pond for commuter terminal prior to discharge to Muddy Bridge Branch | 1 (2/12/93) | deicing/anti-icing[a] | Peak (2/13/93) |
| | | 2 (2/26/93) | anti-icing/deicing[b] | Composite (2/27/93) |
| | | 3 (10/20/93) | rain | Composite (10/21/93) |
| | | 4 (10/26/93) | rain | Peak and Grab (10/27/93) |

[a]Deicing fluids (Type I) used at BWI airport are ethylene glycol based.
[b]Anti-icing fluids (Type II) used at BWI airport are propylene glycol based.

AR 037692

WREC for MDE bioassay testing. Daphnids were <24 h old and fathead minnows <14 d old at the beginning of all tests.

*Test methods*

The 48-h, static renewal acute tests used two replicates per test treatment and 10 organisms per replicate. A dilution series was tested ranging from 100 to 10% storm-water sample, with a dilution factor of 0.56. For the 2nd deicing/anti-icing event, a dilution series down to 1% storm water was used due to rapid toxicity of the storm water seen at a 10% dilution. Tests were conducted at 25°C (±1°C) with a 16-h light:8-h dark cycle. Test protocols were those used by the WREC for its MDE NPDES biomonitoring program. These protocols were developed at the WREC and are consistent with the EPA's acute effluent test protocols [4]. To reduce sample size, daphnids were tested in screened chambers contained in the 400-ml fish test chambers. This technique is currently used in all acute bioassay tests conducted for MDE.

Organisms were fed immediately prior to the start of the test but not during the 48-h test period. Because of the high oxygen demand of the deicing/anti-icing mixtures, all replicates, including controls, were aerated slowly during the tests to ensure adequate dissolved oxygen (>4.0 mg/L). The control/dilution water used in all tests was from a nonchlorinated deep well and is the same as that used in the MDE NPDES biomonitoring program.

Dissolved oxygen (YSI DO meter, Yellow Springs Instrument Co., Yellow Springs, OH), pH (Beckman pH meter, Fullerton, CA), conductivity (YSI conductivity meter), hardness (EDTA titrimetric method), and alkalinity (potentiometric titration method) were measured in the sample and the diluent water prior to the beginning of the test and prior to the 24-h renewal. Temperature was recorded continuously in one replicate during all tests using a probe connected to a chart recorder (Cole-Parmer Instrument Co., Niles, IL). Dissolved oxygen and pH were measured in one replicate of each treatment at the beginning of the test, at 24 h (prior to and after renewal), and at the end of the test.

The endpoint of the tests for both species was mortality. Test chambers were checked for early mortality during the first few hours of the test. The number of surviving organisms in each test chamber was recorded every 24 h during the test.

*Chemical analyses*

Samples from each event were analyzed for a number of chemical constituents, including various glycols. Only the 100% discharge samples were analyzed; this was done by Martel Laboratories (Baltimore, MD) and Artesian Laboratories (Newark, DE) under contract with MES. Appropriate QA/QC procedures were employed for all samples. The well water used for control/dilution water is routinely analyzed for priority pollutants because it is used for the MDE NPDES biomonitoring program. Significant concentrations of the chemical constituents listed below have not been found in this water. All analytical methods followed guidelines outlined in "Methods for Chemical Analysis of Water and Waste" [5]. Methods for individual constituents are as follows: Biochemical Oxygen Demand—405.1; Total Suspended Solids—160.2; Chemical Oxygen Demand—410.4; Ammonia Nitrogen—350.1; Total Kjeldahl Nitrogen—351.3; Total Phosphorus—365.3; Fats, Oils, and Grease—413.1; Total Petroleum Hydrocarbons—418.1; Cadmium—213.2; Chromium—218.2; Copper—220.2; Lead—239.2; Nickel—249.2; Zinc—289.2; Total Toxic Organics—8240, 8250, 8270, 624, and 625. Total Toxic Organics were analyzed only on the peak sample from Site No. 1 for Event No. 2. Analyses included both volatile organic compounds and base neutral/acid extractable compounds. The various glycol species were analyzed by direct injection (2 μl) of the sample into a gas chromatograph (FID detector). The method was developed by Martel Laboratories.

*Statistical analysis*

A 48-h LC50 and a 95% confidence interval were both calculated for each test species where possible. The LC50 was calculated using the moving average angle method since the distribution of mortalities in the tests did not meet the requirements for probit analysis [4].

*Events*

*1st Quarter.* Two deicing/anti-icing events were sampled during the first quarter. The first event was February 12, 1993. This event was mostly morning ice and light snow, followed by significant amounts of rain. Temperatures were above freezing. Airport personnel deiced planes throughout the morning of the event. There were high flows and significant dilution of the deicing/anti-icing mixture. Three bioassays were started on February 13, 1993. Composite and peak bioassays were started on samples from Site No. 1, while a peak bioassay was started from Site No. 4. The peak sample from Site No. 1 was collected from 1130 to 1245 h, while the composite was collected from 0930 to 2145 h. The peak sample from Site No. 4 was collected from 0800 to 0945 h.

The second event was a major snow event, with ice and snow throughout the day on February 26, 1993. Temperatures were below freezing, and there was heavy deicing/anti-icing activity. Very little rain fell during this event, so there was very little dilution of the deicing/anti-icing mixtures. All of the deicing/anti-icing was conducted at the main terminal (Site No. 1), including the commuter flights. Deicing/anti-icing occurred throughout the day but was most concentrated during the heavy morning aircraft activity. Bioassays were started on February 27, 1993, on peak and composite samples from Site No. 1 and on a composite sample from Site No. 4 since there appeared to be no real peak in color or refractometer reading in any of the individual samples from this site. The peak sample from Site No. 1 was collected from 0700 to 0915 h, while the composite was collected from 0700 to 1845 h. Composite sample from Site No. 4 was collected from 1200 to 2345 h. Mortality occurred almost instantaneously in both the peak and composite samples from Site No. 1, so additional dilutions were added to the series (lowest treatment was 1% sample/99% dilution water).

*2nd and 3rd Quarters.* There were no usable storm events during the 2nd quarter. A usable event is one in which runoff from our two sample sites occurred for a 12-h period.

There were a few short-term thunderstorms during the 2nd quarter but nothing that would give both an initial peak runoff sample and a 12-h composite sample.

The lack of precipitation over the summer and early fall and the lack of access to the samplers after dark on the airport property caused problems in trying to sample storm-water runoff at the airport. There were two usable events during the 3rd quarter but they could not be sampled. During the first event there were problems in the morning, and we were unable to start the samplers to catch the initial peak sample. The second event started early in the morning when we could not get on the airport property to start the samplers.

*4th Quarter*. Because there were problems with lack of precipitation and airport access during the 3rd quarter, it was decided to start the samplers whenever there was an event during the day, even if all 12 h could not be sampled. The initial 1- to 2-h runoff from any event should be the most toxic since any water-soluble toxic components would be washed from the pavement in this time period. Two events were sampled during the month of October, one of which represents a reasonably long event (6 to 8 h) and one representing a short event (2 to 3 h).

On October 20, 1993, a rain event occurred that started in the morning. This event will be referred to as Event No. 3. The samplers were started about an hour after the hard rain began to fall. Both peak (1000–1400 h) and composite (1000–1800 h) samples were collected from Site No. 1, and a composite (1030–1830 h) sample was collected from Site No. 4 for this event. Because of a delivery problem, chemical analyses were only conducted on the two composite samples from this event.

On October 26, 1993, an event began in the late afternoon, and the compositors were started prior to any rainfall. This is Event No. 4 for the project. The major precipitation during this event occurred during the first 2 h, and very little sample was collected over the next 10 h. This represents a good peak sample at Sites No. 1 (1700–1900 h) and No. 4 (1700–1900 h), but no composite since the event was so short. A grab sample was also collected at 1030 h on October 27, 1993, from the holding pond drained by the discharge at Site No. 4. The rain event had ended but there was still some flow from the storm-water holding pond. The sample was collected just upstream from sample Site No. 4. This sample was collected because it appeared to be heavily contaminated with fuel and was draining into Muddy Bridge Branch. The fuel was not noticed in the pond prior to the event when the samplers were started.

Three bioassays were started on October 21, 1993 (Event No. 3). Composite and peak bioassays were done on samples from Site No. 1, while a composite bioassay was done on Site No. 4. Three additional bioassays were started on October 27, 1993, from Event No. 4. Peak sample bioassays were started from both Sites No. 1 and 4. An additional bioassay was started on the grab sample taken on October 27, 1993.

## RESULTS AND DISCUSSION

### General

Water quality data for all experiments, including controls, are given in Table 2. The DO and pH values are presented for the control treatments and an average value for all test treatments. Conductivity, alkalinity, and hardness were only measured in the control treatment and 100% test sample. Fish weights and lengths at test end and the fish ages at the start of each test are given in Table 3. The KCl reference tox-

Table 2. Water chemistry data summary for all tests[a] (mean ± SD except for pH, which are the extremes of all measurements)

| Site No. | Event No. | Sample date-type[b] | Dissolved oxygen (mg/L) | pH | Conductivity (μmho) | Alkalinity (mg/L as $CaCO_3$) | Hardness (mg/L as $CaCO_3$) |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 2/13-Cont | 8.5 (0.17) | 7.34–7.73 | 290 (14) | 115 (14) | 62 (3) |
| | 1 | 2/13-Peak | 7.9 (0.94) | 6.52–7.89 | 225 (21) | 73 (4) | 30 (3) |
| | 1 | 2/13-Com | 8.2 (0.33) | 6.36–7.91 | 120 (0) | 38 (4) | 28 (8) |
| | 2 | 2/27-Cont | 8.6 (0.25) | 7.42–7.67 | 298 (19) | 118 (25) | 75 (7) |
| | 2 | 2/27-Peak | 8.1 (0.66) | 7.17–8.00 | 540 (0) | 520 (0) | 800 (0) |
| | 2 | 2/27-Com | 7.7 (1.10) | 6.92–7.83 | 400 (0) | 310 (0) | 880 (0) |
| | 3 | 10/21-Cont | 7.4 (0.74) | 8.19–8.48 | 305 (7) | 158 (4) | 64 (0) |
| | 3 | 10/21-Peak | 6.7 (1.15) | 7.36–8.61 | 178 (4) | 43 (4) | 66 (3) |
| | 3 | 10/21-Com | 6.7 (1.09) | 7.65–8.61 | 173 (4) | 38 (4) | 66 (3) |
| | 4 | 10/27-Cont | 7.8 (0.62) | 8.03–8.31 | 263 (18) | 110 (7) | 66 (9) |
| | 4 | 10/27-Peak | 6.7 (1.46) | 7.50–8.18 | 180 (0) | 38 (4) | 62 (3) |
| 4 | 1 | 2/13-Peak[c] | 8.0 (0.54) | 5.91–7.86 | 120 (14) | 30 (7) | 46 (11) |
| | 2 | 2/27-Com | 8.2 (0.39) | 6.33–8.01 | 2000 (100) | 110 (9) | 168 (29) |
| | 3 | 10/21-Cont | 7.7 (0.44) | 8.12–8.48 | 305 (7) | 158 (4) | 64 (0) |
| | 3 | 10/21-Com | 6.8 (1.09) | 7.19–8.36 | 315 (7) | 118 (11) | 142 (3) |
| | 4 | 10/27-Peak | 7.5 (0.77) | 7.11–8.04 | 373 (4) | 155 (28) | 162 (3) |
| | 4 | 10/27-Grab | 7.4 (0.86) | 6.78–8.06 | 313 (4) | 120 (21) | 138 (9) |

[a]Conductivity, alkalinity, and hardness on 100% treatments only.
[b]Date is when test started; year = 1993; sample type is Cont(rol), Peak, Com(posite), or Grab.
[c]The same controls were used for Site Nos. 1 and 4 when tests started on the same day unless indicated.

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Table 3. Fish (*Pimephales promelas*) information for all tests

| Date | Site No. | Final weight [mg wet wt. (± SD)] | Final length [mm (± SD)] | Age at start (d) |
|---|---|---|---|---|
| 2/13/93 | 1 & 4 | 0.9 (0.31) | 6.3 (0.35) | 4 |
| 2/27/93 | 1 | 8.1 (2.39) | 11.2 (1.00) | 13 |
| | 4 | 6.6 (2.31) | 10.5 (0.97) | 11–12 |
| 10/21/93 | 1 | 4.4 (0.63) | 9.5 (0.53) | 6–8 |
| | 4 | 2.2 (0.76) | 7.6 (0.70) | 7 |
| 10/27/93 | 1 & 4 | 3.5 (1.36) | 8.3 (0.76) | 8–10 |

icity tests conducted for the months of these tests indicated acceptable 48-h LC50 values for both test species.

*1st Quarter winter storm events*

For the first event, the color of the most concentrated sample at Site No. 1 was light pink to medium pink, indicating the presence of diluted deicing/anti-icing mixture. There was no color apparent at Site No. 4, although deicing/anti-icing had occurred at the commuter terminal. Refractometer readings on the samples from this event showed some glycols present in all samples. For the second event, both the composite and peak samples from Site No. 1 were bright, fluorescent pink in color. Refractometer measurements indicated that total glycol in these samples was an order of magnitude more concentrated than in samples from Event No. 1. The sample from Site No. 4 again showed no color and a slight refractometer reading, indicating little or no deicing/anti-icing mixture present in the sample.

The LC50 values for all tests are presented in Table 4 as percent of the 100% storm-water sample. There were no control organism mortalities in any test. Results from the first event indicate some toxicity in both the peak and composite samples from Site No. 1. The LC50 values ranged from 34.3% for the fathead minnow in the peak sample to 69.3% for the daphnid in the composite sample. There was some toxicity from the peak sample from Site No. 4 (100% sample killed 50% of the daphnids but no fathead minnows), but not enough to calculate an LC50. Results from the second event indicate samples from Site No. 1 were much more toxic than Site No. 1 samples collected during Event No. 1, with LC50 values for both species between 1.0 and 2.0%.

The difference in toxicity between the two events would be expected if the glycols were causing the toxicity since concentrations were much higher during the second event (Table 5). Total ammonia levels were also higher during the second event. Analyses conducted by the WREC at the start of the toxicity tests found that the peak sample from Site No. 1 had 32 mg/L total ammonia while the composite sample had 40 mg/L. At the pH and temperature of the samples during the tests, this converts to 0.71 mg/L and 0.56 mg/L un-ionized ammonia for the peak and composite samples, respectively. These levels of un-ionized ammonia are below the species mean acute values (SMAV) for the fathead minnow and daphnid given in the EPA's water quality criteria for ammonia [6]. The *Pimephales promelas* and *Daphnia magna* SMAVs are 2.07 and 1.91 mg/L, respectively. Thus, it does not appear that ammonia is the toxic component in these samples, especially at the dilution levels used in the second event.

The composition of the deicing/anti-icing mixture was different in the two events (Table 5). Samples from the first event contained primarily ethylene glycol (80% of total glycols) with a little propylene glycol and even less diethylene glycol. Samples from the second event contained a much greater percentage of propylene glycol. Because glycol was measured in only the 100% sample and not in any of the other toxicity test treatments, the LC50 values presented below are estimates based on concentrations calculated from these 100% values.

When the LC50 values are based on total glycol concentration, the LC50 was greater (less toxicity) for the first event than for the second event (Table 6). Hartwell et al. [2] found

Table 4. Acute toxicity information on effluents (%) from BWI Airport for all events

| | 48-h LC50 as % effluent (95% C.I.) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Site No. 1 | | | | Site No. 4 | | | | | |
| | Peak | | Composite | | Peak | | Composite | | Grab | |
| Event No. | Fathead[a] | Daphnid[a] | Fathead | Daphnid | Fathead | Daphnid | Fathead | Daphnid | Fathead | Daphnid |
| 1 | 34.3 (28.6–40.1) | 54.8 (47.4–65.4) | 63.5 (58.3–70.0) | 69.3 (59.8–85.3) | NT[b] | 100[c] | –[d] | – | – | – |
| 2 | 1.1 (1.0–1.3) | 1.7 (1.0–1.9) | 1.5 (1.0–1.6) | 1.7 (1.0–1.9) | – | – | NT | NT | – | – |
| 3 | NT | NT | NT | NT | – | – | NT | NT | – | – |
| 4 | NT | NT | – | – | NT | NT | – | – | NT | 26.2 (19.2–34.7) |

[a]Fathead minnow (*Pimephales promelas*); Daphnid (*Daphnia magna*).
[b]NT = not toxic (no mortality in 100% storm-water treatment).
[c]Estimated (50% of the organisms died in 100% treatment, 40% died in the 56% treatment).
-, Test not conducted.

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Table 5. Glycol chemistry data summary of measurements made on the 100% storm-water samples

| | | | | Concentration in sample (mg/L) | | | |
|---|---|---|---|---|---|---|---|
| Site No. | Event No. | Date sampled | Sample | Ethylene glycol | Diethylene glycol | Propylene glycol | Total glycol |
| 1 | 1 | 2/12/93 | Peak | 13000 | ND[a] | 2800 | 15800 |
| | 1 | 2/12/93 | Composite | 6600 | 300 | 1700 | 8600 |
| | 2 | 2/26/93 | Peak | 98000 | 2900 | 130000 | 230900 |
| | 2 | 2/26/93 | Composite | 31000 | 1500 | 85000 | 117500 |
| | 3 | 10/20/93 | Composite | ND | ND | ND | ND |
| | 4 | 10/26/93 | Peak | 22 | ND | ND | 22 |
| 4 | 1 | 2/12/93 | Peak | 790 | ND | 180 | 970 |
| | 2 | 2/26/93 | Composite | 95 | ND | 180 | 275 |
| | 3 | 10/20/93 | Composite | ND | ND | ND | ND |
| | 4 | 10/26/93 | Peak | 11 | ND | ND | 11 |

[a]ND = Nondetectable (detection limit for this method is 1 mg/L). The coefficient of variation for 5 runs of a 100-mg/L sample was 12.5%.

propylene glycol anti-icer mixtures to be more toxic than ethylene glycol deicer mixtures when tested in the laboratory. Our findings from actual storm-water samples support this, since the LC50s based on total glycol showed the samples from the second event, which contained a greater percentage of propylene glycol, to be more toxic than samples from the first event.

There is some indication from the literature that the glycols may not explain all of the toxicity of these mixtures [4,5]. Our findings show that LC50s based on total glycol are substantially lower than what would be predicted from the pure glycol toxicity data [1] (Table 7). Hartwell et al. [2] found that laboratory-derived LC50 values for the deicing and anti-icing mixtures used at BWI airport were also lower (more toxic) than those reported in the literature for the pure glycols. In laboratory studies, Pillard [3] found that formulated ethylene and propylene glycol deicing and anti-icing mixtures were substantially more acutely and chronically toxic than pure ethylene and propylene glycol.

A number of additives are contained in these solutions, including diethylene glycol, ethylene oxide, acetaldehyde, dioxane, high-molecular-weight polymers, polyamines, triazoles, and ureas [2]. In addition, corrosion and rust inhibitors such as sodium nitrate, sodium benzoate, borax, and benzotriazole are commonly added. All, or some, of these additives may be responsible for the increased toxicity of the mixtures as compared to the toxicity that would have been predicted from the pure glycol toxicity data [2,3].

Samples from these tests were analyzed for a number of different chemical parameters (Table 8). None of these parameters appear to be present at levels that individually would explain the toxicity seen in Event No. 2. The toxic organics analysis for the peak sample from Site No. 1 for this event indicated no detectable compounds except for phenol, at a concentration of 110 $\mu$g/L. The level of phenol present was 1 to 2 orders of magnitude below the EPA acute toxicity values for the daphnid and fathead minnow [7]. Because all treatments for the first two events had to be aerated to maintain dissolved oxygen, the results of these toxicity tests do not reflect possible acute toxicity from BOD and COD, which were elevated in the samples containing glycols (Table 8). For example, the COD of these samples was extremely high (270,000 mg/L in the peak sample of Event No. 2).

It is also interesting to note the high levels of total nitro-

Table 6. Acute toxicity of effluents from BWI Airport during deicing/anti-icing events based on mg/L total glycol[a]

| | 48-h LC50 as mg/L total glycol (95% confidence limits) | | | | | |
|---|---|---|---|---|---|---|
| | Site No. 1 | | | | Site No. 4 | |
| | Peak | | Composite | | Peak | |
| Event No. | Fathead[b] | Daphnid[b] | Fathead | Daphnid | Fathead | Daphnid |
| 1 | 5,408 (4,488–6,333) | 8,666 (7,486–10,326) | 5,461 (5,013–6,019) | 5,960 (5,147–7,334) | NT[c] | 970[d] |
| 2 | 2,589 (1–3,091) | 3,988 (1–4,425) | 1,753 (1–1,924) | 2,003 (1–2,216) | NT | NT |

[a]Total glycol measured only in 100% sample (concentrations in each treatment were based on the dilution factor and represent nominal values).
[b]Fathead minnow (*Pimephales promelas*); Daphnid (*Daphnia magna*).
[c]NT = not toxic (no mortality in 100% storm-water treatment).
[d]Estimated (50% of the organisms died at 970 mg/L, 40% died at 543 mg/L).

AR 037696

Table 7. Review of the relevant acute toxicity information on glycols as pure compounds [1]

| | Organism age and test type | LC50/EC50 Values (mg/L) | Reference |
|---|---|---|---|
| Ethylene glycol | | | |
| *P. promelas* | Fry (12 mg); 96-h LC50 (s,n)[a] | 53,000 | [8] |
| | Juvenile (77 mg); 96-h LC50 (s,n) | 49,000 | [8] |
| | Subadult (391 mg); 96-h LC50 (s,n) | 57,000 | [8] |
| | No age given; 96-h LC50 (s,n) | >10,000 | [9] |
| *D. magna* | <48 h neonate; 48-h EC50 (s,m) | 50,450 | [10] |
| | <24 h neonate; 48-h LC50 (s,n) | 46,300 | [11] |
| | <24 h neonate; 48-h LC50 (s,n) | 51,100 | [11] |
| | <24 h neonate; 48-h LC50 (s,n) | 46,300 | [12] |
| | Age not reported; 48-h LC50 (s,n) | >10,000 | [9] |
| 1,3-Propylene glycol | | | |
| *D. magna* | <24 h neonate; 24-h LC50 (s,n) | 8,285 | [13] |
| | <24 h neonate; 48-h LC50 (s,n) | 7,417 | [13] |
| 1,2-Propylene glycol | | | |
| *D. magna* | <24 h neonate; 24-h LC50 (s,n) | >10,000 | [13] |
| | <24 h neonate; 48-h LC50 (s,n) | >10,000 | [13] |
| Diethylene glycol | | | |
| *P. promelas* | Juvenile (35 d); 96-h LC50 (f,m) | 75,200 | [14] |
| *D. magna* | <24 h neonate; 24-h LC50 (s,n) | >10,000 | [15] |

[a]Test methods (s = static, f = flow-through; n = nominal concentrations, m = measured concentrations).

gen found in the samples from Event No. 2 (380 mg/L in the peak and 400 mg/L in the composite – Table 8). The airport uses urea to deice the runways and pavement areas. While these levels of nitrogen are not likely to be acutely toxic unless most of the nitrogen is in the form of ammonia, these discharge levels represent a substantial loading to Kitten Branch. During a severe winter, large amounts of urea could be applied for deicing, resulting in high total nitrogen loads from the airport. It should be noted that at a site in Kitten Branch approximately 0.5 mile downstream from the discharge from Site No. 1, total nitrogen was only 21 mg/L in a composite sample taken during Event No. 2. This decrease in total nitrogen may be due to either dilution from other runoff or to the fact that there was a large beaver dam upstream from this site that could have blocked much of the initial flow.

### *4th Quarter rain events and fuel spill*

There was no toxicity from any of the peak or composite samples collected from Sites No. 1 and 4 for either Events

Table 8. Chemistry data summary of measurements made on the 100% storm-water samples[a]

| | | | Concentration in sample (mg/L)[b] | | | | | | | | Concentration in sample ($\mu g/L$)[c] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Site No. | Event No. | Date-type[d] | BOD | COD | TSS | $NH_3$ | TKN | P | Oil | TPH | Cd | Cr | Cu | Pb | Ni | Zn |
| 1 | 1 | 2/12-Peak | 6,700 | 24,000 | 11 | 1 | 33 | 39 | 2 | | | | | | | |
| | 1 | 2/12-Com | 6,400 | 11,000 | 21 | ND | 30 | 12 | 2 | | | | | | | |
| | 2 | 2/26-Peak | 42 | 270,000 | 21 | 10 | 380 | 60 | 29 | | ND | ND | ND | ND | ND | 1,430 |
| | 2 | 2/26-Com | 3 | 170,000 | 31 | 23 | 400 | 48 | 29 | | | | | | | |
| | 3 | 10/20-Com | 21 | 72 | 12 | ND | 1.1 | 0.2 | ND | ND | ND | 1 | 31 | 4 | 5 | 240 |
| | 4 | 10/26-Peak | 64 | 120 | 13 | ND | 1.7 | 0.5 | 7.4 | ND | 3 | ND | 45 | 16 | 4 | 191 |
| 4 | 1 | 2/12-Peak | 1,900 | 2,700 | 20 | 1 | 21 | 6 | 2 | | | | | | | |
| | 2 | 2/26-Com | 138 | 700 | 28 | 5 | 26 | ND | 14 | | | | | | | |
| | 3 | 10/20-Com | 16 | 52 | 14 | ND | ND | 0.1 | ND | ND | ND | ND | 9 | 1 | 5 | 60 |
| | 4 | 10/26-Peak | 11 | 20 | 31 | ND | ND | 0.2 | 9.5 | ND | 1 | ND | 3 | 11 | 5 | 35 |
| | 4 | 10/27-Grab | | | | | | | | 28 | | | | | | |

[a]ND = nondetectable; blank spaces = constituents not analyzed in specific samples.
[b]BOD (biochemical oxygen demand); COD (chemical oxygen demand); TSS (total suspended solids); $NH_3$ (ammonia nitrogen–detection limit = 1.0); TKN (total Kjedahl nitrogen–detection limit = 1.0); P (total phosphorus–detection limit = 0.02); Oil (oil and grease–detection limit = 5.0); TPH (total petroleum hydrocarbons–detection limit = 4.0).
[c]Cd (cadmium–detection limit = 0.5); Cr (chromium–detection limit = 1); Cu (copper–detection limit = 1 by ICP); Pb (lead–detection limit = 1); Ni (nickel–detection limit = 1); Zn (zinc–detection limit = 14).
[d]Sample type is Peak, Com(posite), or Grab. All samples taken in 1993.

No. 3 or 4 (Table 4). Chemical analyses on the October 20, 1993, event (Event No. 3) indicated no detectable levels of ammonia, oil and grease, petroleum hydrocarbons, or ethylene or propylene glycol in any of these samples (Tables 5 and 8). Samples from the October 26, 1993, event (Event No. 4) indicated no ammonia or petroleum hydrocarbons from either Site 1 or Site 4 (Table 8). Site No. 1 had 7.4 mg/L oil and grease and 22 mg/L ethylene glycol but no propylene glycol. Site No. 4 had 9.5 mg/L oil and grease and 11 mg/L ethylene glycol (Table 5) but no propylene glycol. These concentrations of ethylene glycol were not toxic, as would have been predicted from the results of our earlier winter tests during Events 1 and 2.

Significant mortality occurred in the daphnid test from the fuel-spill grab sample taken on October 27, 1993 (Table 4). A 48-h LC50 of 26.2% (95% confidence limits of 19.2 and 34.7%) was calculated. Many of the daphnids were trapped in a surface layer in all of the treatments, except the controls, after 24 h. At the end of the test, all trapped daphnids were examined and found to be dead, not immobilized. The sample was not toxic to the fathead minnow. Personnel from MES and BWI airport returned to this site later in the day in an unsuccessful attempt to determine the source of the fuel. The smell of fuel was still strong at that time. Chemical analysis of the initial sample taken at 1030 h contained 28 mg/L total petroleum hydrocarbons (Table 8). An additional sample taken later in the day (1600 h) contained 17 mg/L total petroleum hydrocarbons.

## CONCLUSIONS

Samples from both winter storm events (Events No. 1 and 2) caused acute toxicity to both the fathead minnow and the daphnid. Samples from the second event showed a very toxic runoff, with LC50 values for both species in the 1.0 to 2.0% effluent range. Our results indicate that most of the toxicity is due to the various glycols used but that other components of the deicing/anti-icing mixtures may contribute some toxicity. The second event probably represents a "worst case" event since there was a lot of deicing/anti-icing occurring and very little precipitation present for dilution. From discussions with MES and airport officials it appears that the flow from discharge Site No. 1 represents significantly more than 1% of the flow of Kitten Branch.

Samples from the rain events during which no deicing/anti-icing activity occurred did not cause acute toxicity problems at either discharge point. It is apparent from our grab sample results that under certain circumstances (i.e., fuel spills) acutely toxic discharges could be released from the airport property, regardless of whether deicing or anti-icing mixtures are being used.

Two additional points should be mentioned. Because these tests eliminated low dissolved oxygen as a test condition in the deicing/anti-icing samples, BOD and especially COD impact on the streams needs to be considered. If the deicing and anti-icing fluids are treated prior to any discharge, this should remove the BOD and COD. Additionally, the high levels of total nitrogen from the use of urea is another potential problem occurring during winter storm events.

Since this study has been completed, MDE has issued a new NPDES permit for BWI. This permit contains requirements for implementing plans for the collection and recycling and/or treatment of the deicers and anti-icers. These plans call for the construction of contained deicing/anti-icing stations located near the ends of the runways with a system of pumps, piping, and storage for used fluids. Prior to the construction of this collection/treatment system, all runoff containing deicing/anti-icing mixtures will be collected by truck and treated elsewhere. The continuous evaluation of existing controls and testing of new technologies to further prevent pollution is also required as Best Management Practices for this facility. During the first year of the new permit BWI must also evaluate the use of sodium formate as a runway deicer and possible replacement for urea. Finally, BWI will also be required to develop an overall storm-water pollution prevention plan.

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AR 037699