Chapter 16

How to Develop Chemical Criteria for Airport Stormwater

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Airport stormwater management has been an issue of national and international concern for several years with considerable focus directed to the impact of de-icing activities on runoff quality. In Canada, the principle statute for effluent quality management is the Fisheries Act. This report focuses on the statute fundamentals and, from them, developing chemical limits for runoff quality that will enable airport management to meet the intent of the Act (no fish lethality at the end of the pipe) with confidence.

This presentation will consider the aquatic toxicity data from effluents reflecting collective airport activities (gates, de-icing pads, taxi ways, runways) chemical measurements (glycol, ammonia, nitrite, petroleum hydrocarbons), the relationship of biological oxygen demand (BOD) materials to dissolved oxygen concentrations in receiving waters, and aesthetic considerations of colour. Chemical limits for all these are recommended, based on the products used, to permit airport managers to consistently comply with all aspects of the Fisheries Act.

16.1 Introduction

Airport stormwater has received considerable attention because airport operations represent a unique application of industrial chemicals which in the past were not well controlled or treated. The chemicals in airport stormwater are

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predominantly present during winter de-icing seasons to remove ice and snow from airlines and runways in order to protect passenger and crew safety. Focus has most often been directed towards the glycol-based de-icers because of the high visibility and volume of application.

Ice, snow, or frost on wing surfaces disrupts the air flow over lift and control surfaces of an aircraft. The consequence of this roughness, as low as 0.36 mm, is severe lift lost and impaired manoeuvrability. De-icers remove and retard the development of ice on lift surfaces and are critical to airline operation for safety reasons.

De-icing fluids are composed of water, ethylene or propylene glycol as freeze point depressants, corrosion inhibitors, wetting agents and dye. Salts are not used as freeze point depressants as they tend to be corrosive. Lower molecular weight organic freeze point depressants are not used as flammability becomes a potential problem. The effectiveness of the freeze point depressant decreases as the molecular weight increases, therefore restricting the use of the higher molecular weight glycols. Typically, glycol makes up about half the formulation, the additives account for less than 0.5%, and the water takes the balance.

Aircraft de-icing fluids are applied hot (80°C) and at fairly high pressure to melt and dislodge the frozen deposits. The low freezing point of the de-icing fluid (-43°C) will prevent re-freezing in the absence of precipitation.

The residual film of de-icing fluid on aircraft surfaces is thin. Continuous precipitation dilutes the fluid and can cause the diluted glycol solution to freeze. When precipitation rates are high or at airports where time between departure from the gate and takeoff are long, anti-icing fluid is applied. Anti-icing fluids are similar to de-icing fluids in composition except for small amounts of thickener. Anti-icing fluids are usually applied at low pressure and in small quantities to aircraft surfaces which are free of frozen deposits. Anti-icing fluid can also be applied as a preventative coating. This practice can significantly reduce the total amount of fluid used. Anti-icing fluids also prevent return of aircraft for repetitive de-icing in severe weather.

Over the past several years as effluent controls were put in place for different industry sectors, other commercial operations came under closer examination, among them airports. A number of stormwater studies were conducted in the U.S.A. (Hartwell *et al*, 1995; Pillard, 1996) and Europe that indicated effluents could be toxic to fish and benthic communities. There was also considerable speculation that dissolved oxygen was reduced as a result of high measures of BOD being reported from glycol presence.

16.1.1 Surface Water and Effluent Guidelines

Recent focus on the use of de-icers resulted in the Canadian government developing an airport stormwater effluent guideline for glycol within the Canadian Environmental Protection Act (CEPA) of 100 mg/L total glycol (Canada

Gazette, 1994). This guideline was developed in 1994 by consensus among government and industry parties within the context of interim Canadian Council of Ministers of the Environment (CCME) (1994) surface water guidelines at the time of 3 mg/L for ethylene glycol, 74 mg/L for propylene glycol and 31 mg/L for diethylene glycol. These CCME guidelines are currently under review and the latest drafts indicated interim numbers heading towards 192 mg/L for ethylene glycol and 520 mg/L for 1,2-propylene glycol while the data set for diethylene glycol is considered inadequate to support even an interim guideline. Further, consideration of diethylene glycol controls is unnecessary in the context of aircraft de-icing as it is only a trace constituent of current de-icing formulations.

16.2 Environmental Needs

In order to deal with effluent quality effectively within the context of environmental safety it is essential to take a holistic approach. Environment Canada established an end of the pipe guideline limit for “glycol” in order to encourage better management of de-icers and anti-icers at airports. Airport managers, however, are responsible for total effluent quality and must consider other factors contributing to toxicity, physical and aesthetic impairment of receiving waters.

The applicable legislation in Canada is the Fisheries Act which prohibits the discharge of a substance that is deleterious to fish or fish habitat. Generally the deleterious nature of a substance is accepted when effluent regulatory samples produce lethality in fish or invertebrate tests. In other cases when permit limits are exceeded, concentrations of chemicals above provincial or federal surface water guidelines or objectives are used as evidence of deleterious conditions. This evidence has proven persuasive in litigation but in reality, often exaggerates the harmful nature of the effluent, if any, in the receiving water.

16.2.1 Key Issues

The key issues in receiving water quality related to airport runoff are:

- whether toxicants are present in toxic concentrations,
- whether there is adequate oxygen present in receiving waters to sustain aquatic life, and
- whether the physical quality of the receiving water is affected, specifically colour, temperature, solids.

16.2.2 Effluent Objectives

This results in defining specific objectives for effluent quality:

- effluents must meet the test of non-lethality ($LC50 \geq 100\%$ for trout and *D. magna*)

- dissolved oxygen must meet specific fisheries criteria
- temperature must be within 10 °C of ambient
- solids must not affect water quality (toxicity) or habitat (alter ecological niches)
- colour must not affect visibility or aesthetic appreciation
- turbidity must be $\leq 10\%$ above background

16.2.3 Chemicals that Affect Environmental Quality

Airports use a number of different types of chemicals that can find their way to stormwater. These include glycols from aircraft de-icing operations, urea and acetate based runway de-icers, and various petroleum hydrocarbons (fuels, lubricants, cleaners).

These chemicals can be toxic to fish and invertebrates at appropriate concentrations. Glycol is the major constituent contributing to the BOD load from aircraft de-icing and anti-icing operations.

Some runway de-icers contain urea, which will contribute to effluent toxicity due to urea breakdown products such as ammonia, nitrate, and nitrite. Other runway de-icers use potassium acetate, calcium magnesium acetate and sodium formate which do not exhibit the same toxicity as urea breakdown products, but will contribute somewhat to BOD.

16.3 Aquatic Toxicity

16.3.1 De-icers

Glycol based de-icers are conventionally manufactured with about 50% ethylene glycol or propylene glycol plus less than 0.5% additives with the balance being water. Each manufacturer modifies the constituents of their de-icing formulation to differentiate their product from competitors and introduce improvements over time. The effects of these changes of formulation even with the fairly tight proportions described above can result in significant differences in aquatic toxicity. Table 16.1 demonstrates differences between two ethylene glycol products from different manufacturers and between propylene versus ethylene based glycol products.

In the case example above, the glycol de-icer with the highest LC50 is the least toxic because a higher concentration is required to produce the same lethality to trout as is produced with the other products at lower equivalent glycol concentrations. The toxicity data above is expressed both as the concentration of “formulated product” that produces lethality or non-lethal and as the concentration of glycol in that “formulated” concentration. Typically glycol represents 54% to 57% of the formulated product.

Table 16.1 Glycol-toxicity (mg/L).

	Aircraft De-Icer					
	Brand AE (UCAR XL54)		Brand BE		Brand P	
	Form- ulated	as Glycol	Form- ulated	as Glycol	Form- ulated	as Glycol
LC50	32,600	17,600	18,200	9,820	3,530	2,014
Non Lethal	20,440	11,040	12,400?	6,700?	2,500	1,425

AE & BE = ethylene glycol based de-icer
P = propylene based de-icer

Urea is often used as a runway de-icer which generates ammonia, nitrite and nitrate as degradation products. Ammonia and nitrite are both very potent aquatic toxicants. Furthermore, the dynamic of ammonia is that the toxic form of ammonia increases with increasing temperature and pH of the exposure conditions. If one uses a generic set of conditions that is typical of Great Lakes basin and prairie lowland airports (pH 8.0 and winter water temperature of 5°C), a total ammonia concentration, for example 2 mg/L (the target value would change with different environmental conditions), can be determined as a level below which there would be no aquatic toxicity as illustrated in Table 16.2 below:

Table 16.2 Non-lethal total ammonia (mg/L) - (IJC, 1984).

	Temperature °C		
	0	5	10
pH 7.5	9.6	6.4	4.3
pH 8.0	3.1	2.0	1.4
pH 8.5	1.0	0.7	0.5

Another degradation product of urea is nitrite which is generally considered to be transient but in fact is sufficiently stable to cause acute lethality to aquatic life over several days of exposure. Nitrite toxicity is mitigated by the presence of chloride ion which will be dependant on the balance of locally available salts and melt water or rain water which is typically very dilute. Table 16.3 demonstrates the high toxicity of nitrite to trout and the mitigating effect of chloride ion.

Table 16.3 Nitrite toxicity (Lewis, 1986)

	Cl ⁻ < 1 mg/L	Cl ⁻ 20 mg/L
Trout LC50 (mg/L)	0.15-0.70	4.6-13.6

16.3.2 Petroleum Hydrocarbons

Petroleum hydrocarbons can be released from many different sources within airport operations including, refuelling, servicing (lubrication and cleaning), low level leakage from storage systems or aircraft. Petroleum hydrocarbons take many different chemical forms and the characteristics can change through the volatilization ageing process so it is impossible to define specific concentrations that are problematic as is the case for the chemicals cited above. However, there are a number of reports which either relate fish toxicity to a specific fuel (Connell and Miller, 1981) or document lethal conditions coincident with non-specific hydrocarbon concentrations. The following data (Table 16.4) provides some guidance as to levels of petroleum hydrocarbons that are consistent with non-lethality to trout.

Table 16.4 Petroleum hydrocarbon toxicity.

Fuel Oils	1-10 mg/L	LC50 tolerant fish species	(Connell and Miller, 1981)
	0.1-1.0 mg/L	LC50 sensitive fish species	(Connell and Miller, 1981)
Pet. HCs	6.9 mg/L	non-lethal to RBT	(BAR, 1996)
	8.7 mg/L	non-lethal to RBT	(BAR, 1996)
	7.4-28 mg/L	non-lethal to FHM	(Fisher et al, 1995)
	10.2 mg/L	LC50 to FHM (NH3 present)	(Fisher et al, 1995)
Conclusion: < 7 mg/L likely non-lethal to rainbow trout.			
RBT = rainbow trout			
FHM = fathead minnow			

16.4 Aesthetics - Colour

Colour will be relevant when commercial products used at airports contain dyes that can be visible in runoff. Typically, the type and visibility of the dye present will be product specific therefore will have to be determined for each product and cross referenced to a co-indicator. In the case of de-icing products the appropriate co-indicator is glycol. In the case of one product evaluated a series of de-icer solutions were prepared and a panel of observers described the various solutions compared to reference tap water sample. The following range of responses (Table 16.5) indicated that for this particular product dilutions containing concentrations of ethylene glycol below 2250 mg/L would not appear different from lab tap water.

Table 16.5 Glycol - aesthetics (colour).

Brand AE (mg/L) (as ethylene glycol)	Panel Description
9000	Light orange
4500	Slight light orange tinge
2250	No difference from lab water
920	No difference from lab water
92	Colourless
9	Colourless

16.5 Dissolved Oxygen Requirements

Aquatic life require certain minimum oxygen concentrations to complete their life cycles and the U.S. EPA has provided specific guidance according to the duration of exposure. This approach recognizes that while it is desirable to have higher long term average oxygen concentrations aquatic organisms can accommodate short depressions from that long term average. Table 16.6 provides different limits for oxygen in water recognizing also that warm water species are slightly more tolerant of depressed oxygen conditions than cold water species like salmonids.

Table 16.6 Limits for dissolved oxygen mg/L (EPA, 1986).

	Description			
	Cold Water Species		Warm Water Species	
	Early Life Stage	Other	Early Life Stage	Other
30-Day Mean	NA	6.5	NA	5.5
7-Day Mean	9.5 (6.5)	NA	6.0	NA
Minimum	NA	5.0	NA	4.0
1 Day Minimum	8.0 (5.0)	4.0	5.0	3.0

() = interstitial oxygen levels in gravel substrate

The above data indicate that for short term periods (seven continuous days) both warm water and cold water fish species would not be harmed if the dissolved oxygen levels were at or above 5 mg/L. Generally, the concentration of contaminants will be highest at the beginning of a runoff event (Snodgrass, 1977) so if the BOD from glycol is less than would effect a dissolved oxygen drop to 5 mg/L at any time, then the rest of the runoff period would have a lesser impact in the receiver.

16.6 Glycol Limits

The amount of glycol that can be discharged to a receiving stream without the dissolved oxygen being depressed below 5 mg/L is likely dependent on factors such as precipitation dilution available from the surrounding watershed, the temperature of the receiving waters, the presence and reactivity of bacteria present in the aquatic system, the load of oxygen within precipitation runoff and upstream dilution waters. In order to address the question of the maximum amount of glycol (either ethylene or propylene) that could be accommodated by a receiving stream while meeting the dissolved oxygen target of 5mg/L the assumptions outlined in Table 16.7 were adopted:

Table 16.7 Glycol - dissolved O₂.

Objective: Dissolved O ₂ > 5 mg/L for fish survival
Assumptions:
No "acclimatization" lag time
Initial oxygen in runoff is 90% saturation
Ambient temperature 4°C
No algal oxygen contributions from photosynthesis
No other oxygen consumption terms (i.e. BOD, respiration)
No sediment oxygen demand
Ice cover eliminates surface re-aeration
1.29 mg of oxygen is required to degrade 1 mg of ethylene glycol
1.69 mg of oxygen is required to degrade 1 mg of propylene glycol

The above assumptions were then incorporated into a simplified Streeter-Phelps equation to solve for various concentrations over various residence periods for both of the glycols used to manufacture de-icing products:

$$DO = DO_0 - 1.29C(1 - e^{-kt}) \quad (16.1)$$

where:

- DO = dissolved oxygen concentration (mg/L);
- DO₀ = initial dissolved oxygen concentration (mg/L);
- C = ethylene glycol concentration (mg/L);
- k = decay rate (1/day); and
- t = time (days).

For propylene glycol the 1.29 constant is replaced with 1.69 in the above equation.

The output of the above calculation for ethylene glycol is presented in Figures 16.1 while the same calculation for propylene glycol is presented in Figure 16.2.

Figure 16.1 Maximum ethylene glycol concentration for >5 mg/L DO under precipitation or watershed dilution at 4°C.

Figure 16.2 Maximum propylene glycol concentration for >5 mg/L DO under precipitation or watershed dilution at 4°C.

The decay rates for ethylene glycol ($0.033 \cdot d^{-1}$) were determined from BOD decay data generated by Union Carbide (1997) while propylene glycol decay rates ($0.043 \cdot d^{-1}$) were taken from data in Verschoren (1983).

These graphs show that, allowing for at least 10 dilutions of oxygen-rich upstream water being available to stormwater runoff, the discharge concentrations of ethylene glycol could be as high as 1800 mg/L and propylene glycol could be as high as 1300 mg/L without the dissolved oxygen being depressed below 5 mg/L over a 24 hr residence time. Of course a further assumption was that after that 24 hr period, there would be adequate opportunity for additional dilution within a running stream environment to offset any additional oxygen consumption required for the final degradation of the remaining glycol.

16.7 Consolidation of Data

The above assessments of the potential effects of individual chemicals leads to developing a stormwater runoff chemical profile that could be discharged from airports and meet the previously described objectives:

- effluents must meet the test of non-lethality ($LC50 \geq 100\%$ for trout and *D. magna*),
- dissolved oxygen in receivers must be ≥ 5 mg/L, and
- colour must not affect visibility or aesthetic appreciation.

In fact the concentrations of toxicants selected in the evaluation were consistent with *no mortality of fish* which provided additional protection than the regulatory requirement of no more than 50% mortality of fish. The collective chemical limits would of course be dependent on the type of de-icer products used at an airport (constituent formulation and type of glycol) and would be as presented in Table 16.8.

Table 16.8 Maximum concentrations (mg/L) to meet operational objectives.

	Toxicity (non-lethal)	Dissolved O ₂ (DO > 5 mg/L)	Aesthetics (no objection)
Glycol (Brand AE)	11,040	1800	2250
Glycol (Brand BE)	6700	1800	?
Glycol (Brand P)	1425	1300	?
Ammonia (Total)	<2.0	NA	NA
Nitrite (Cl ⁻ <1 mg/L)	<0.2	NA	NA
Petroleum HCs	<7.0	NA	?

The concentrations of ammonia, nitrite and petroleum hydrocarbons would be common in all cases but in the case examples presented above the glycol limit would be 1800 mg/L for the ethylene products and 1300 mg/L for the propylene product with the dissolved oxygen objective being the most limiting requirement. Toxicity is not limiting for the ethylene based de-icers but represents an almost equivalent limitation as the oxygen objective for the propylene product .

16.8 Process for Developing Chemical Criteria for Stormwater

This study identifies the following procedural steps that can be applied to any stormwater application to meet site specific or generic needs:

- establish performance objectives,
- characterize environmental conditions,
- determine dilution available,
- identify compounds/chemicals present,
- select chemical indicator parameters,
- determine toxicity of compound (per unit indicator),
- determine DO effect (per unit indicator),
- determine aesthetics effects (per unit indicator), and
- select indicator levels to meet performance objectives.

References

- B.A.R. Environmental Inc. 1996. An evaluation of standard acute toxicity test for airport wastewater/effluent associated with de-icing activities. Report to Environment Canada, Transport Canada and the Airline Transport Association of Canada.
- Canada Gazette. 1994. Order in Council. Department of Environment. Glycol guidelines. Canada Gazette, Part I , February 5, 1994.
- CCME. 1994. Appendix XVI. Canadian water quality guidelines: Updates (March 1994) Ethylene glycol, diethylene glycol and propylene glycol. pp8. Canadian Council of Ministers of the Environment. Winnipeg, Manitoba.
- Connell, D.W. and G.J. Miller. 1981. Petroleum hydrocarbons in aquatic ecosystems-behaviour and effects of sublethal concentrations: Part 2. CRC Critical Reviews I Environmental Control 12: 105-162.
- EPA. 1986. Quality criteria for water 1986. Dissolved oxygen. United States Environmental Protection Agency, Office of Water Regulations and Standards, Washington, D.C. U.S.A.

- Fisher D.J., M.H. Knott, S.D.Turley, B.S. Turley, L.T. Yonkos, G.P.Ziegler. 1995. The acute whole effluent toxicity of storm water from an international airport. *Envir. Tox. Chem.* 14:1103-1111.
- Hartwell, S.I., D. M. Jordahl, J.E.Evans, E.B.May. 1995. Toxicity of aircraft de-icer and anti-icer solutions to aquatic organisms. *Envir. Tox. Chem.* 14: 1375-1386.
- IJC, 1985. Report of the Aquatic Ecosystem Objectives Committee - 1985 Annual Report., International Joint Commission, Windsor, Ontario, Canada.
- Lewis, W.M. 1986. Toxicity of nitrite to fish: a review. *Trans. Am. Fish. Soc.* 115: 183-195.
- Snodgrass, W.J. 1977. Hamilton harbour study 1977. Material input to Hamilton harbour. Report to Ontario Ministry of Environment, Water Resources Branch, Toronto, Ontario.
- Pillard, D.A. 1996. Assessment of benthic macroinvertebrate and fish communities in a stream receiving storm water runoff from a large airport. *J. Fresh. Ecology* 11:51-59
- Union Carbide. 1997. Ecological aspects of UCAR® aircraft deicing/anti-icing fluid ULTRA+ and ethylene glycol. Technical Bulletin. 2/3/97. Pp7. Union Carbide, Danbury, Connecticut, USA.
- Verschuere, K, 1996. Handbook of environmental data on organic chemicals. 3rd Ed. Van Nostrand Reinhold Company Inc. New York.