

**Canadian Soil Quality Guidelines for Propylene Glycol:  
Environmental and Human Health**

**Discussion Document**

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## Note to Readers

Scientific supporting documents are routinely prepared to provide the background and rationale for the development of Canadian Environmental and Human Health Soil Quality Guidelines for substances potentially released to the environment. This preliminary discussion document was intended to assist the Canadian Council of Ministers of the Environment (CCME) Soil Quality Guidelines Task Group (SQGTG) ascertain whether there is a need for a Canadian soil quality guideline for propylene glycol (PG). In particular, this discussion document summarizes what is known about releases of PG to the Canadian environment, its post-release environmental fate, and best available information on toxicity to humans or other living organisms.

Pursuant to deliberations by the SQGTG in 2004, it was decided not to formally derive a set of Canadian soil quality guidelines for PG at this time, since the major environmental issues associated with PG releases are best dealt with through other management mechanisms and tools. Readers should be aware that this is not intended as a scientific supporting document *per se*.

For additional technical details regarding this preliminary discussion document, please contact:

Doug A. Bright, Ph.D.  
Senior Environmental Scientist  
UMA Engineering Ltd.  
200-415 Gorge Rd. E.  
Victoria, British Columbia  
V8T 2W1

Tel. 250-475-6355  
e-mail [dbright@umagroup.com](mailto:dbright@umagroup.com)

*or*

Environment Canada  
Water Priorities Branch  
National Guidelines and Standards Office  
351 St. Joseph Blvd.  
Gatineau, Quebec  
K1A 0H3

Tel. 819-953-1550  
FAX 819-953-0461  
[ceqg-rcqe@ec.gc.ca](mailto:ceqg-rcqe@ec.gc.ca)

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## 1. INTRODUCTION

Canadian Soil Quality Guidelines are numerical concentrations or narrative statements that specify maximum concentrations of potentially toxic substances in soils beyond which there may be risks to human health or the environment. The guidelines are specifically recommended to protect and improve environmental quality, and maintain human health risks from environmental contamination at acceptably low levels. Guidelines, once developed and refined, are endorsed through the Canadian Council of Ministers of the Environment (CCME).

The CCME Soil Quality Guidelines Task Group (SQGTG), comprised of one representative each from the Canadian Provinces and Territories, as well as a representative from Health Canada and Environment Canada, each year nominates new substances for guidelines development. Propylene glycol was nominated in 2003 for the possible development of soil quality guidelines, based in large part on its use in aircraft de-icing fluids, and subsequent release to the Canadian environment, within the immediate vicinity of Canadian airports.

This document does not directly support the development of Canadian soil quality guidelines for propylene glycol; rather, it is intended as a preliminary discussion document. The report briefly describes –

1. what propylene glycol is, its major uses, and sources of release to the Canadian environment;
2. post-release environmental fate, including distribution and persistence; and
3. effects on humans, other mammals, other vertebrates, soil invertebrates, plants and other organisms.

As discussed further on, the major concern surrounding the use and release of aircraft de-icing fluids is associated with entrainment in storm water or surface water runoff and potential risks for aquatic life. Canadian water quality guidelines for propylene glycol (PG) have been previously endorsed by the CCME. This preliminary discussion document provides an assessment of soil concentration thresholds of PG that could lead to exceedences of the Canadian water quality guidelines.

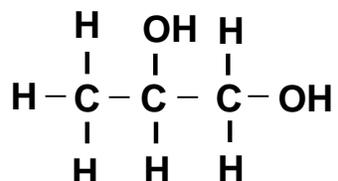
This document also provides a discussion of the available toxicological information for various receptor groups relative to toxicity data needs for deriving Canadian soil quality guidelines, as described in “A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines” (CCME, 2003; currently in draft).

This brief review augments similar reviews prepared by the World Health Organization, International Programme on Chemical Safety (WHO, 1994), the U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR, 1997), and other agencies.

## 2. BACKGROUND INFORMATION

### 2.1 Physical and Chemical Properties

Propylene glycol (PG) belongs to a group of organic chemicals named dihydric or aliphatic alcohols, which are characterized by two hydroxyl (OH<sup>-</sup>) functional groups attached to methyl subunits in an aliphatic chain. The physical and chemical properties of PG are presented in Appendix I.



Some synonyms of PG include the following –

- 1,2-propylene glycol
- alpha-beta-dioxypropan
- alpha-propylene glycol
- dowfrost
- methylethylene glycol
- methylglycol
- monopropylene glycol
- PG 12
- propandiol-1.2
- propane-1,2-diol
- propylene glycol USP
- trimethyl glycol

Propylene glycol may be manufactured by treating propylene with chlorinated water to form the chlorohydrin which is converted to the glycol by treatment with sodium carbonate solution. It is also prepared by heating glycerol with sodium hydroxide (USFDA, 2003).

Propylene glycol is a clear, odourless, tasteless, relatively non-volatile, viscous liquid with a melting point of -59° C and a boiling point of 188.2° C (USFDA, 2003). Propylene glycol has a low vapour pressure of 0.07 mm Hg at 20° C and a low Henry's law constant of  $1.7 \times 10^{-7} \text{ atm}\cdot\text{m}^3\cdot\text{mole}^{-1}$ , hence it is relatively non-volatile. It is miscible in water and has an octanol/water coefficient of -0.92; therefore, bioaccumulation is not expected to be significant.

Propylene glycol is similar to ethylene glycol in many of its chemical properties; however, the two do not share a similar degree of toxicity in mammals (propylene glycol has a much lower mammalian toxicity; see section 2.2). Ethylene glycol has been formally assessed in Canada as a Priority Substance under the Canadian

Environmental Protection Act (CEPA, 2000) and a set of Canadian Soil Quality Guidelines were developed for ethylene glycol in 1997 for revision and adoption in 1999 (CCME, 1999).

## **2.2 Production and Uses in Canada**

Propylene glycol (CAS No. 57-55-6) is a synthetic liquid with some similarities to other alcohols. PG readily dissolves in water, and is miscible with methanol, ethanol, acetone, chloroform, and other organic solvents. PG, therefore, can act as a solvent or carrier for a larger number of limited solubility substances. It also has a high latent heat capacity; i.e. can hold large amounts of heat before boiling, and can depress the freezing point of aqueous solutions. PG is hygroscopic (has a strong tendency to absorb water) and has been used as an industrial humectant (moistening agent). PG can also be used as a building block (monomer) for polymers such as polypropylene glycols and polyester compounds.

The United States Food and Drug Administration (USFDA) has classified propylene glycol as an additive that is “generally recognized as safe” (GRAS) for use in food; therefore, it is used extensively to absorb extra water and maintain moisture in certain medicines, cosmetics, or food products (USFDA, 2003). PG is also used as a solvent for food colors and flavors. Because of its solvent properties, PG is used extensively in the paint and plastics industries. PG has also been used in the United States to create artificial smoke or fog used in fire-fighting training and in theatrical productions.

PG has been used extensively in the cryoprotection of germ cells, embryos, and other cryopreserved tissues or cell cultures.

There has been no manufacturer of PG in Canada since the DOW Chemical Plant in Sarnia, Ontario, ceased production in 1992. At the time of its closure, the DOW Plant was producing approximately 16 kilotonnes per year. Presently, Canada imports an average of 20 kilotonnes per year. By comparison, the United States utilizes approximately 400 kilotonnes per year (Camford 2000).

There are two major markets in Canada which account for almost 80% of the total usage of PG: polyester resins and consumables (food, cosmetics and tobacco). The remainder is said to be ‘miscellaneous’, including use in paints, antifreeze and animal feeds. There has been a notable increase in the amount of PG used in the production of antifreeze and aircraft deicing/anti-icing fluids (ADFs), driven in part by environmental/toxicological concerns associated with ethylene glycol.

## **2.3 Sources to the Canadian Environment**

Propylene glycol is not on the National Pollutant Release Inventory in Canada, nor the Toxic Release Inventory in the US. Therefore, there is little data available on any releases of PG into the environment.

### **2.3.1 Processing Plants**

There has been no manufacturer of PG in Canada since the DOW Chemical Plant in Sarnia, Ontario, ceased production in 1992. Importers of PG may create by-products with high concentrations of PG during processing, but effluent from those plants is not expected to be disposed of into the environment untreated or in large quantities.

### **2.3.2 Airports**

De-icing/anti-icing fluids are routinely applied to aircraft at most Canadian airports during the winter months, in order to prevent ice formation on critical surfaces prior to take-off. The typical seasonal limits of de-icing activities in Canada are from October to April of each year, although airports in subarctic and arctic regions may have a requirement for de-icing in any month of the year. Some of the arctic airports lacking a paved apron and capture area merit special attention with regard to the release of de-icing/anti-icing fluids.

Aircraft de-icing fluids (ADFs) can be composed of either ethylene or PG (or both), as well as water, thickener, and additives. ADF formulations are proprietary; however, the most common type of ADF for application to most aircraft contains approximately 65% glycols, 33% water and 2% additive (US EPA, 2000)

According to Corsi *et al.* (2001, 2003), three types of ADFs have been approved in the United States and are being used to de-ice and prevent ice formation on aircraft. The situation in Canada is very similar, since the major suppliers are from the United States. Type I formulations are used to melt and remove snow and ice accumulations from aircraft but provide little protection from further accumulations. Types II, III and IV are specifically designed to prevent icing, and contain additives polymers and other thickening agents that provide anti-icing protection on previously de-iced aircraft during pre-flight activities and takeoff. In addition, mixtures of ethylene glycol and urea, potassium acetate, potassium formate, or sodium formate are commonly used to protect airport taxiways and runways from snow and ice. Type III fluids are no longer produced or available for purchase from US suppliers.

Each ADF type uses a proprietary formulation “additive package”. Several researchers have demonstrated that the additives in ADFs may be contributing to environmental risks. For example, Corsi *et al.* (2003) identified the presence of alkylphenol ethoxylates (APEOs) in the majority of nine ADF samples tested. Among the APEOs detected was nonylphenol ethoxylate (NPE), which has well-demonstrated endocrine disruptor tendencies. Cancilla *et al.* (1997, 2003) demonstrated that much of the aquatic toxicity of ADFs was attributable to the presence of benzotriazole and tolyltriazoles, added as rust inhibitors. Breedveld *et al.* (2003) demonstrated that triazoles released with ADFs tend to be highly mobile in water and tend to be persistent.

Volumes of PG used annually at Canadian airports appear to be less than the use of ethylene glycol. However, Vancouver International Airport has noted a change in the

ratio of ethylene glycol (EG) to PG in ADF mixtures over the last 10 years, increasing from 90/10 to 50/50 EG/PG. Propylene glycol-based ADFs are said to have a lower freezing point than ethylene glycol-based ADFs, although generally require a higher percentage of glycol.

#### *2.3.2.1 Application*

The application process of ADFs to aircraft varies with each airport authority. Each application of ADF to a commercial airliner may involve from 600 to 4,000 L of ADF. An estimated 4,000 to 16,000 L of ADF may be required to de-ice a large commercial airliner during severe weather conditions (US EPA, 2000).

Facilities such as Vancouver, Lester B. Pearson, Moncton and Edmonton International airports have designated areas for de-icing. These typically consist of a purpose-built concrete pad and associated piping or channelling to divert water and waste glycol to the municipal sewer/storm water system, or to retention ponds for off-site treatment and disposal. Recent upgrades at some facilities have included the placement of synthetic liners underneath the concrete de-icing pads. In contrast, facilities such as Calgary, Winnipeg and Saskatoon International have no centralized de-icing area, and allow de-icing/anti-icing operations to commence on most concrete pad surfaces. The glycol waste endpoint is also the municipal sewer and/or storm water system.

It was approximated by the US EPA (2000) that during de-icing only 20% of ADFs applied actually adhere to an aircraft, and only 5% remain by the time the craft is ready for takeoff. This implies that about 80% of ADF is lost at the de-icing pad, and an additional 15% is lost along the taxiways and runways.

#### *2.3.2.2 Collection and Disposal*

There are three dominant strategies for handling and disposing of over sprayed glycol at airports in Canada: vacuum collection, channeling into sanitary sewers, and channeling into storm sewers. Other solutions include the discharge into wetlands, and on-site treatment and recycling.

'Pink Snow' is the term used to describe the fallen snow on deicing areas, which has soaked up the glycol from the ground (which generally is pink in colour due to added dyes). Disposal of the pink snow also varied between airports, and includes vacuum collection, channeling into storm sewers, and stockpiling in designated areas.

#### *2.3.2.3 Volumes Used*

Glycol ADF usage at International airports varies from year to year, and is dependant on the winter weather conditions. Based on a phone survey with environmental managers from seven airport authorities, during the 2002/2003 winter season there was approximately 104,000 L of PG-based ADF used. It should be noted that this represents only a portion of the 42 airports that are currently members of the Canadian

Airport Council, and actual volumes of PG utilized could differ significantly. Refer to Appendix II for survey details of the volumes used.

### 3. ENVIRONMENTAL FATE

#### 3.1 Soil

Soil factors affecting the fate and behaviour of PG in the terrestrial environment are pH, organic matter, clay content, cation exchange capacity, aeration and texture. The major processes that determine the mobility and distribution of PG in the terrestrial environment are partitioning into surface and ground water given the high aqueous solubility, as well as rapid biodegradation and photolysis. Volatilization and sorption to soils are fate processes with only minor importance.

Propylene glycol is approximated to have a half-life in soil due to biodegradation equal to or less than that in water (from 1 to 5 days). However, degradation rates will vary with soil properties, temperature and other environmental conditions.

ATSDR (1997) estimated the half-life of propylene glycol in water to be 1 to 4 days under aerobic and 3 to 5 days under anaerobic conditions, assuming first order kinetics. The half-life in soil is expected to be equal to or slightly less than that for water.

Soil temperature potentially has a large influence on PG biodegradation rates. Klecka *et al.* (1993) evaluated the effects in microcosms of substrate concentration and temperature on the microbially-mediated loss rates of five different ADFs, which included ethylene glycol, PG, and diethylene glycol. The soil was a sandy loam with 2.8% organic carbon content. High levels of glycols were not inhibitory to biodegradation, and all three glycols degraded rapidly in soils with starting concentrations ranging from 390 to 5,300 mg/kg (the soils were collected from an area adjacent to a runway in Michigan). Complete biodegradation for soils with lower initial concentrations (~400 ppm PG) occurred after about 11 days; however, a soil with a starting concentration of approximately 3,300 ppm (w:w) PG showed a loss at 8° C of about 76% over a 111 d period (leaving a remaining concentration of approximately 800 ppm). The initial degradation appeared to follow zero-order kinetics; i.e. the rate of loss was independent of the initial starting concentration at levels above 100 ppm w:w. Average degradation rates were in the range of 66 to 93 mg/kg soil/day at 25° C; 20 to 27 mg/kg soil/day at 8° C.; and only 2.3 to 4.5 mg/kg soil/day at -2° C. Environmental temperature is a major factor influencing biodegradation rates, therefore.

No information was found on concentrations of PG in soil within a field setting.

#### 3.2 Water

Propylene glycol is highly soluble in water, and readily metabolized by microbes and higher organisms once released into the environment. The biodegradation process

requires oxygen; therefore, dissolved oxygen (DO) concentrations in receiving waters may be negatively impacted following a glycol release.

ADF additives may cause adverse effects to the biodegrading microorganisms, thereby slowing the degradation process. Research results of a propylene-based ADF containing tolyltriazole in water had a degradation rate approximately three-times lower than for pure PG.

Bielefeldt *et al.* (2002) examined secondary effects of PG introduction to soils on groundwater flow using 15 cm saturated sand columns. Rapid PG biodegradation was found to be accompanied by a decrease in the saturated hydraulic conductivity by one to three orders of magnitude, likely as a result of bacterial biomass build-up around soil particles.

### **3.3 Air**

Propylene glycol is not expected to readily volatilize into air from water, due to its high solubility and low vapour pressure. If released into the atmosphere during high temperatures, PG should exist almost entirely in the vapour phase and undergo rapid photochemical oxidation. The half-life for this reaction has been estimated to be 20-32 hours.

### **3.4 Assisted Degradation**

Propylene glycol in effluents from propylene glycol production plants (none in Canada) or from ADFs entrained in surface run-off contain very high biological oxygen demand/chemical oxygen demand (BOD/COD) loads. Two methods for treatment of waste water or storm water containing propylene glycol (ATSDR, 1997) include a methane fermentation process and a biotreatment process that uses mixed cultures of bacteria to degrade the compound.

Vesper *et al.* (1994) developed a bench-scale method of the treatment of propylene glycol in low-permeability subsurface soils. The technique involves the hydraulic fracturing of soils, followed by injection of sodium percarbonate encapsulated in polyvinylidene chloride, which results in the slow release of oxygen and enhanced aerobic biodegradation.

## **4. TOXICITY**

### **4.1 Mammals**

There have been numerous studies regarding the toxicological effects of PG in mammals (Appendix IV). Given that PG is relatively non-toxic to mammalian species, a complete review of mammalian toxicology is not included herein. The interested reader is referred to WHO (1994), ATSDR (1997), and NTP (2003).

The majority of research has been focused on the use of PG in food, cosmetic and pharmaceutical products. The U.S. FDA has ruled that PG is an additive that is “generally recognized as safe” (GRAS) for use in food substances. Dosage studies involving mammals indicate that PG had no effect on fertility and reproduction in multiple generations of Swiss mice at up to  $10 \times 10^3 \text{ mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$  (USDA, 2002).

Considerable oral and dermal toxicity data exist for ethylene glycol, since accidental ingestion by humans and other mammalian species is quite common. PG, however, is considerably less acutely toxic than ethylene glycol. The principal difference between the two substances is that ethylene glycol, when metabolized in mammalian systems, leads to the accumulation of metabolites such as glycolic acid, oxalate, and lactic acid. Glycolic acid, and to a lesser extent, lactic acid, contribute to the production of metabolic acidosis, which is one of the hallmarks of acute ethylene glycol intoxication. The principle metabolites of PG include D-lactate, glucose, and  $\text{CO}_2$ . Like ethylene glycol, PG causes acidosis, through conversion to lactic and pyruvic acids. However, the acidosis from PG is not as severe as that caused by ethylene glycol.

In spite of the number of formal toxicological studies of PG, there are still concerns about high exposures in especially young infant humans. For example, Peleg *et al.* (1998) reported a clinical case of propylene glycol intoxication in a premature infant, who went into a state of coma after treatment for burns with antiseptic dressings. Cessation of the topical treatment resulted in complete recovery. Urine analysis showed a high level of PG in the infant. Macdonald *et al.* (1987) commented that small infants receiving intravenous nutrition may experience PG dose in excess of the World Health Organization Allowable Daily Intake of 25 mg/kg/d, and this might be related to increased incidence of cardiorespiratory distress.

Ballard *et al.* (2000) showed that amending cattle diets with an energy supplement containing 17% PG increased milk yield. No negative effects of the energy supplement, were found. PG is used as a drench in the livestock industry to treat for ketosis, or to increase fertility (Miyoshi *et al.*, 2001).

## 4.2 Aquatic Life

Although the direct toxicity of PG is relatively low, indirect effects on aquatic life are common at release sites. Glycols may require oxygen to biodegrade (although anaerobic biodegradation is also potentially rapid), and aquatic toxicity may increase as a result of the creation of anaerobic conditions during periods of warm water temperatures. It should be noted that ADFs are diluted with water, and therefore will exert a lower biological oxygen demand than pure glycol.

Toxicological data collected for PG in the environment has been based mainly on fresh water and marine environment studies involving aquatic species. Price *et al.* (1974) conducted laboratory studies where brine shrimp were exposed over 24 h to PG in salt water. The observed  $\text{LC}_{50}$  was greater than  $1.0 \times 10^4 \text{ mg}\cdot\text{L}^{-1}$ . Bridie *et al.* (1979) also

conducted acute toxicity studies on Goldfish and determined that concentrations greater than  $5 \times 10^3 \text{ mg}\cdot\text{L}^{-1}$  were required prior to mortality (EPA 2004).

While toxicity studies generally show ethylene glycol and PG to be fairly non-toxic in an aquatic environment, ADF toxicity is significantly higher. This increase has been attributed to the additives in ADFs, including surfactants, corrosion inhibitors and flame retardants. Exact concentrations and compositions of additives in ADFs is proprietary information. Surfactants (such as nonylphenol ethoxylates) are generally 0.5% by volume ADF, and corrosion inhibitors and flame retardants (such as tolytriazole) constitute up to 0.5% by volume ADF. Nonylphenol ethoxylates have been indirectly shown to produce a known endocrine disruptor during degradation (hydrophobic nonylphenol), which could cause interference with reproduction and growth of aquatic organisms and humans.

### 4.3 Soil Biota

There have been a limited number of studies involving the toxicity of PG on terrestrial plants, most notably *Lactuca sativa* (lettuce) (Appendix III). Lettuce test results from Pillard and Dufresne (1999) compare favorably to the results from previous studies by Reynolds (1977). Reynolds reported germination  $\text{EC}_{50}$  for lettuce of  $50,540 \text{ mg}\cdot\text{L}^{-1}$ , which was very similar to the emergence  $\text{IC}_{50}$  of  $49,330 \text{ mg}\cdot\text{L}^{-1}$  in Pillard's study. Pillard also measured NOEC and LOEC endpoints for seedling emergence of both lettuce and perennial ryegrass (*Lolium perenne*). He recorded soil concentrations of 4,500 and  $15,000 \text{ mg}\cdot\text{L}^{-1}$ , respectively for lettuce, and 15,000 and  $50,000 \text{ mg}\cdot\text{L}^{-1}$ , respectively, for ryegrass (Pillard 1999). A 1993 study (Hulzebos 1993) of the acute (7-14 days) effects of PG on *Lactuca sativa* population biomass, indicated an  $\text{EC}_{50}$  greater than  $1,000 \mu\text{g}\cdot\text{g}^{-1}$  soil.

Castro *et al.* (2000) examined the phytoremediation of triazole-containing ADFs using grass or sunflowers. They found a threshold for toxicity of triazoles in these plants of about 0.1 g/L in the watering solution applied to a vermiculite/soil mixture. The authors had difficulties growing sunflowers, however, when the irrigation water concentration approached or exceeded about 4% ADF (9.2 g/L of glycol). This was speculated to be a result of the propylene glycol present.

The majority of data on PG toxicity to plants is of limited value for establishing environmentally protective soil thresholds, since the studies were based on exposures from liquid media, rather than from spiked or field collected soils.

The review of available literature did not indicate any published studies involving PG toxicity to soil invertebrates.

## 5. ANALYTICAL METHODS

The analytical methods employed for the quantification of PG are similar to that for ethylene glycol. Gas chromatography (GC) with an FID or MS detector are routinely used. For GC quantitation, glycols must first be derivatized by prior acidification and then esterification. Glycol esters are then transferred to an organic solvent prior to injection on the column. High performance liquid chromatography (HPLC) is also a commonly used technique.

The preferred method for the determination of ethylene glycol in soils is the extraction with water and analysis using GC in combination with flame ionization detection (GC/FID). According to ATSDR (1997), capillary GC with FID or ECD, possibly followed by MS, generally gives good quantitative results down to the parts per million range, with recovery usually greater than 80%.

EPA direct injection methods 8015b (USEPA Method 8015b) and 8430 (USEPA Method 8430) have been developed for the analysis of PG in water samples. There are no specific standardized methods for soils, but the high aqueous solubility of PG makes it relatively easy to analyze aqueous extracts from soil samples, using these methods.

## 6. EXISTING GUIDELINES AND REGULATIONS

In 1994, under the Canadian Environmental Protection Act (CEPA), Environment Canada published the 'Glycol Guidelines', applicable to federal airports. The Guidelines stipulate that the responsible federal department should ensure the discharge of glycols into surface water resulting from aircraft deicing and anti-icing activities at a federal airport does not exceed a concentration of  $100 \text{ mg}\cdot\text{L}^{-1}$  (Environmental Canada 1994).

The current Canadian Environmental Quality Guidelines specify a value of  $500 \text{ mg}\cdot\text{L}^{-1}$  as protective of freshwater aquatic species (CCME 2003).

From the 17<sup>th</sup> report on the Joint FAO/WHO Expert Committee on Food Additives (1974), the acceptable daily intake (ADI) of PG is established at  $25 \text{ mg}\cdot\text{kg}^{-1}$  body weight.

The ATSDR (1997) has established a Minimum Risk Level (MRL) for humans of 0.009 ppm in air, derived for intermediate-duration inhalation exposure (1.5-364 days) to PG. This was based on a LOAEL of 51 ppm for nasal hemorrhaging (Suber et al. 1989). MRLs were not established for oral or dermal exposure routes owing to the lack of relevant data.

No existing soil quality guidelines for PG were located.

## 7. PRELIMINARY ASSESSMENT OF POSSIBLE SOIL QUALITY GUIDELINES

### 7.1 Human Health

Health Canada has not defined a Tolerable Daily Intake limit for PG. The World Health Organization, however, has established an Allowable Daily Intake (ADI) of 25 mg/kg bw/day.

The preliminary human health soil guideline ( $PSQG_{HH}$ ) is calculated using the following equation:

$$PSQG_{HH} = \frac{(TDI - EDI) \times SF \times BW}{(AF_G \times SIR) + (AF_L \times IR_s) + (AF_s \times SR) \times ET} + BSC$$

where,

$PSQG_{HH}$	=	preliminary human health-based soil quality guideline (mg/kg)
TDI	=	tolerable daily intake (mg/kg bw-day)
EDI	=	estimated daily intake (multimedia exposure assessment) (mg/kg-day)
SF	=	soil allocation factor (unitless)
BW	=	body weight (kg)
BSC	=	background soil concentration (mg/kg)
$AF_G$	=	relative absorption factor for gut (unitless)
$AF_L$	=	relative absorption factor for lung (unitless)
$AF_s$	=	relative absorption factor for skin (unitless)
SIR	=	soil ingestion rate (kg/day)
$IR_s$	=	soil inhalation rate (kg/day)
SR	=	soil dermal contact rate (kg/day)
ET	=	exposure term (unitless)

PG is expected to act as a threshold-acting toxicant. A 0.5 to 5 year old toddler is modeled as the most sensitive receptor, therefore, for agricultural, residential or urban parkland land use areas.

All absorption factors (in the gut, lungs, and across the dermis) were conservatively assumed to be 100% (1.0). Often dermal uptake is assumed to be considerable less than 100% (i.e. 20% or less). In the case of PG, however, the solvent properties suggest a somewhat higher potential for absorption through exposed skin.

The assumed receptor and exposure parameters are shown below:

Parameter	Symbol	Child (0.5 y - <5 y)
Body Weight (kg)	BW	16.5
Air Inhalation Rate (m <sup>3</sup> /d)	IR	9.3
Soil Inhalation Rate (kg/d)	IR <sub>S</sub>	7.1 x 10 <sup>-9b</sup>
Water Ingestion Rate (L/d)	WIR	0.6
Soil Ingestion Rate (kg/d)	SIR	8.0 x 10 <sup>-5</sup>
Skin Surface Area (m <sup>2</sup> )		
- Hands	SA <sub>H</sub>	0.043
- Other	SA <sub>O</sub>	0.258
Dermal Loading to Skin (kg/m <sup>2</sup> -event)		
- Hands	DL <sub>H</sub>	0.001
- Other	DL <sub>O</sub>	0.0001
Soil Dermal Contact Rate	SR	6.9 x 10 <sup>-5</sup>
Dermal Exposure Frequency (events/d)	EF	1

a – all parameters from Richardson, 2003.

b – assumes an average particulate matter concentration of 0.76 µg/m<sup>3</sup>, per USEPA (1992) guidance.

The background PG concentration in soils (EDI) is assumed to be negligible. The soil allocation factor is assumed to be 1. Note that PG exposures via diet, through ingestion of pharmaceuticals or other health care products, or dermally from various topical treatments has not been included in the multi-media exposure calculation (it is assumed to be zero). As will be noted below, however, conclusions about soil PG levels associated with acceptable health risks are likely to be robust, with little sensitivity to assumptions regarding additional types of exposure.

The PSQG<sub>HH</sub> for PG is –

$$PSQG_{HH} = \frac{(25 \text{ mg / kg } \times d) \times 1.0 \times 16.5 \text{ kg}}{(1.0 \times 8.0 \text{ ee} - 5 \text{ kg / d}) + (1.0 \times 7.1 \text{ ee} - 9 \text{ kg / d}) + (1.0 \times 6.9 \text{ ee} - 5 \text{ kg / d}) \times 1} + 0$$

$$PSQG_{HH} = 2.8 \times 10^6 \text{ mg PG/kg soil}$$

$$= \mathbf{2.8 \text{ kg PG/kg soil}}$$

In light of the above, it is concluded that concentrations of PG exceeding 100% w:w soil concentration would not result in unacceptable human health risks.

## 7.2 Nutrient and Energy Cycling

No data were located of relevance to the derivation of a soil threshold for protection of nutrient and energy cycling as an environmental protection endpoint in soils.

### 7.3 Direct Soil Contact

Information on the toxicity of PG in soils was located for only one plant species (lettuce, Appendix III) and no soil invertebrate species. According to CCME (2003), at least ten non-redundant data points from at least three studies, including at least two soil invertebrate and two plant species, are required to calculate a soil contact guideline using a weight-of-evidence approach. For application of the LOEC method, a minimum of three studies reporting LOEC endpoints must be considered, including at least one terrestrial plant and one soil invertebrate study. The LOEC method can be accompanied by use of an uncertainty factor to derive a Threshold Effects Concentration (TEC).

If the minimum data requirements cannot be met for the weight of evidence and LOEC methods, the TEC is derived by extrapolating from the lowest available EC50 or LC50 datum using an uncertainty factor (UF). However, A minimum of three studies must be considered to select the lowest EC50 or LC50, including one terrestrial plant, and one soil invertebrate study.

In light of the lack of data, is not possible to calculate a preliminary soil quality guideline based on direct soil contact (PSQG<sub>SC</sub>). According to CCME (2003), “If minimum data requirements for the above methods cannot be met, then there is insufficient information to develop a final environmental soil quality guideline (SQG<sub>E</sub>). Data gaps will be identified for further research. (see Section 8 herein).

### 7.4 Protection of Aquatic Life based on Groundwater-mediated Transport

The Canadian Water Quality Guideline for Freshwater Life Protection has been established as 500 mg/L. Based on this value, the CCME (2003) groundwater model was used along with default assumptions, in order to arrive at an upper concentration limit of PG in contaminated soil, below which it would be very unlikely that groundwater mediated transport would result in an exceedance of the Freshwater Life guideline at the outflow face into a surface water body.

Default generic site and soil assumptions are described in detail in CCME (2003). In general, it is assumed that a surface water body that is viable habitat for aquatic life occurs at a distance of 10 m from a mass of contaminated soil. Furthermore, assumed site conditions would favour the rapid transport of the contaminant in groundwater, directly toward the surface water body.

Other assumptions or values used to derive a SQG<sub>FL</sub> were –

Log <sub>10</sub> K <sub>OC</sub> :	0.76 mL/g (ASTDR, 1997)
Henry’s Law Constant:	1.7 x 10 <sup>-7</sup> atm.m <sup>3</sup> /mol (ASTDR, 1997)
Half life in the unsaturated zone:	5 days (Section 3.1)
Half life in the saturated zone:	10 days (Section 3.1)

The preliminary SQG<sub>FL</sub> calculated using the groundwater model along with the generic (CCME, 2003) assumptions for a coarse textured soil was **6,210 mg/kg**.

The preliminary SQG<sub>FL</sub> estimate notwithstanding, PG has a very limited tendency to absorb to soil, and movement of PG from soil to groundwater, followed by entry into surface waters, remains a significant concern. For this pathway, calculations based on CCME protocol do not capture the effects of PG release to groundwater and surface water as a result of the very high biochemical oxygen demand (BOD). The Canadian water quality guideline (500 mg/l) for PG from which a soil recommendation is back-calculated doesn't take into account problems associated with oxygen depletion, changes in redox potential, changes in pH, *et cetera*. Therefore, it would be more appropriate for the 500 mg/l water quality guideline to be used in conjunction with a dissolved oxygen guideline; however, this cannot be translated directly into a numerical recommendation for the soil to groundwater pathway.

## 8. CONCLUSIONS

### 8.1 Potential for Entry into the Environment

During de-icing activities at airports, it is likely that ADFs will accumulate on the ground, regardless of collection efforts at the de-icing pads. Since airports are typically located on flat, low-lying areas, the underlying soils are generally well compacted and groundwater movement is low.

As the surface soils begin to melt in the spring, the ADFs can begin to permeate the ground and degrade via natural microbial processes. Due to its high solubility, PG will be highly mobile in soils, and eventually reach ground or surface waters. ADF additives such as benzotriazole may also leach readily into groundwater and surface water, but may degrade more slowly than PG. Alkylphenol ethoxylates, on the other hand, are expected to become more tightly sorbed to soil particles, and may exhibit longer term residual toxicity based on soil-based exposures.

At least two factors might influence environmental persistence. First, ADF additives might interfere with natural degradation processes of glycol by inhibiting microorganisms. Second, biodegradation rates of glycols are expected to be appreciably lower at temperatures near freezing than at higher temperatures.

Using volumes of PG-based ADFs utilized at Canada's International Airports, and the associated PG content of the ADFs, we can estimate an annual volume of PG that may be reasonably expected to reach the environment through spillage and/or planned releases due to airport activities. Phone surveys indicated that approximately 104,000 L of PG-based ADFs was used during the 2002/2003 winter season at seven of 42 non-federal Canadian airports. Based on an average PG content of 65%, and accounting for volumes lost to taxiways, runways and de-icing facilities, it can be estimated that slightly over 19,000 L of PG is introduced to the environment each year from airport activities at these locations. Refer to Appendix II for details and assumptions. Accounting for all airports, the estimated annual loss to the environment from ADF use is probably greater than 100,000 L of PG.

The release of ADFs of the environment might exacerbate groundwater-mediated risks based on either the possibility of co-solvent effects (e.g. increased apparent solubility of hydrocarbons in the presence of glycol co-contamination), or of large changes in subsurface redox conditions (which could further mobilize other substances; e.g., enhanced arsenic leaching from dissolution of iron oxyhydroxides) in light of the rapid microbial utilization of glycols as a carbon source. The conceptual framework behind the Canadian soil quality guidelines does not address such issues; however, airport and environmental managers should be aware of these issues when managing ADF use and the remediation of ADF-affected soils.

## 8.2 Data Deficiencies

Based on the physical and chemical properties of PG, and in light of the literature review, the following conclusions and recommendations are provided:

1. There is sufficient scientific knowledge on the toxicological properties of propylene glycol as it pertains to human or mammalian exposures. Any soil guideline is likely to reflect the fact that PG has been designated as Generally Recognized as Safe for consumption purposes;
2. There is sufficient scientific knowledge on the toxicological properties of propylene glycol as it pertains to aquatic environments. It is this data that formed the basis for the development of the current Canadian Water Quality Guideline for propylene glycol in the context of freshwater life protection. The estimation of soil-groundwater partitioning,  $K_D$  (and transfer to surface water bodies) based on the estimated  $K_{OC}$  may not be as accurate as other estimation methods, and this may limit the accuracy of groundwater model predictions. In addition, the predictions are likely to be sensitive to persistence half-life estimates.
3. There is insufficient scientific data available on the toxicological effects of propylene glycol on terrestrial plants or animals. Therefore, the derivation of an environmental soil quality guideline ( $SQG_E$ ), as stipulated in *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME 2003) is not currently feasible. Some jurisdictions such as the Netherlands support under specific circumstances the use of aquatic organism toxicity data for estimating risks to terrestrial biota in the absence of more directly relevant data; however, there is no theoretical support for such a practice, given the possible differences in autecology, physiology, and modes of toxic action. It is recommended that additional chronic ecotoxicity data for at least three additional plant species and three soil invertebrates be developed if there is an interest in establishing Canadian soil quality guidelines for PG. This may also require the consideration of at least four soil types: a coarse, organic rich sandy loam; a fine organic rich clay; an organic poor coarse textured soil, and organic-poor fine textured soil.

4. There is insufficient information on the effects of PG on soil microbial and fungal processes that in turn influence carbon, nitrogen, phosphorus and other macronutrient cycling in soil ecosystems. It is clear that PG releases tend to enhance the secondary productivity of heterotrophic bacteria in soil, and that PG can be used by microbes as a preferred and highly accessible sole carbon source. Subsidiary effects on other soil microbial processes remain poorly investigated, however. In addition, the current understanding of factors that affect microbial activity at release sites for ADFs is insufficient for the development of strong predictive models.
5. There is good information on the effects of PG on livestock in agricultural settings. A toxicity reference value could be developed in light of past research on PG exposures in drenched cattle, in dairy cows fed PG in energy supplements, and based on studies of other mammalian species. Such an approach is deemed to be of low priority, however. Just as PG is designated as being generally recognized as safe (GRAS) for human consumption, this likely holds true for other terrestrial mammals, including livestock and wildlife. As for humans, risks based on exposures to PG in soil are very unlikely.
6. The ecological or human health risks associated with widespread use of aircraft de-icing/anti-icing fluids in Canada might be driven more by additive substances such as triazoles or alkylphenol ethoxylates (APEOs). Airport and environmental managers in Canada, therefore, need to be aware of the possible presence of these. Canadian soil quality guidelines have been developed for APEOs (CCME 2002).

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## Appendix I Physical and Chemical Properties of Propylene Glycol

Property	Value
CAS Registry	57-55-6
Chemical Formula	C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>
Appearance	Thick, clear, oily liquid
Odor	Odorless
Taste	Tasteless
Solubility	Miscible in water
Specific Gravity	1.035 – 1.037 at 25°C
Molecular Weight	76.11*
Boiling Point	188.2°C (370°F)*
Melting Point	-59°C (-74°F)*
Liquid Density	1.038 g/mL*
Vapor Density (Air = 1)	2.6
Vapor Pressure	0.129 mm Hg at 25°C; 0.07 mm Hg at 20°C*
Evaporation Rate (BuAc = 1)	0.01**
Partition Coefficients	Log Kow: -0.92*; Log Koc: 0.76-0.88*
Stability	Stable under ordinary conditions of use and storage
Hazardous decomposition products	Carbon dioxide, carbon monoxide (when heated); aldehydes, lactic acid, pyruvic acid, acetic acid
Incompatibilities	Strong oxidizing agents
Conditions to avoid	Heat, flames, ignition sources and incompatibles

\* ASTDR, 1997

\*\* Dow, 2003

**Appendix II: Survey Information on Propylene Glycol Volumes Used at Canadian International Airports in 2002/2003**

<i>Airport</i>	<i>Volume of Total ADF (2002 – 2003)</i>	<i>% PG-Based ADF</i>	<i>Approx. Volume of PG –based ADF</i>	<i>Approx. Percentage of PG in ADF</i>	<i>Approx. Percentage lost to Taxiways</i>	<i>Approx. Percentage 'lost' at Deicing Pad (based on type of facility)</i>	<i>Total Volume PG Exposed to Enviro. Per year</i>
Vancouver International	190,000 L	50%	95,000 L	65%	15%	10%	15,500 L
Toronto International	4,000,000 L	0%	0 L	65%	15%	50%	0 L
Calgary International	2,000,000 L	0.0001%	2,000 L	65%	15%	50%	845 L
Edmonton International	500,000 L	1 – 2%	7,500 L	65%	15%	50%	3,200 L
<b>Totals</b>	<b>6,690,000 L</b>	<b>-</b>	<b>104,500 L</b>	<b>-</b>	<b>-</b>	<b>-</b>	<b>19,545 L</b>

**Appendix III: Consulted Terrestrial Plant Toxicity Studies for Propylene Glycol**

<b>Species</b>	<b>Effect</b>	<b>Endpoint</b>	<b>Exposure Duration</b>	<b>Reported Concentration</b>	<b>Notes</b>	<b>Reference</b>
<i>Lactuca sativa</i> (Lettuce)	Germination	EC <sub>50</sub>	72 h	655 mM		Reynolds, 1977.
	Germination	EC <sub>50</sub>	7-14 d	>1,000 mg/kg		Hulzebos <i>et al.</i> , 1989
	Germination	EC <sub>50</sub>	14 d	> 1000 mg/kg		
	Growth	EC <sub>50</sub>	21 d	56 mg/L (CI: 23-140 mg/L)	hydroponic	
	Emergence	EC <sub>25</sub>	5 d	24,760 mg/L	In petri plates (hydroponic)	Pillard and Dufresne, 1999
	Root Length	EC <sub>25</sub>	5 d	9,880 mg/L		
	Shoot Length	EC <sub>25</sub>	5 d	1,190 mg/L		
<i>Lolium perenne</i> (Ryegrass)	Emergence	EC <sub>25</sub>	5 d	24,210 mg/L	In petri plates (hydroponic)	Pillard and Dufresne, 1999
	Root Length	EC <sub>25</sub>	5 d	2,850 mg/L		
	Shoot Length	EC <sub>25</sub>	5 d	3,120 mg/L		

**Appendix IV: Available Mammalian and Avian Toxicity Studies for Propylene Glycol, Excerpted from ATSDR (1997) Unless Indicated Otherwise**

Species	Effect	Endpoint	Exposure Duration	Reported Concentration	Methods	Notes	Reference
Sprague-Dawley rats	Respiratory – nasal hemorrhaging	LOAEL	90 d for 5 d/wk x 6 h/d	51 ppm	Inhalation exposure	mean target aerosol concentrations of 51, 321, or 707 ppm	Suber et al, 1989
	Immunological/Lymphoretical	NOAEL		707 ppm			
Monkeys (Macacus Rhesus)	Respiratory	NOAEL	13 months continuous	112 ppm	Inhalation exposure	No effects seen in gastro., hepatic, renal, or body wt. measures	Robertson et al., 1947
Rat	Respiratory	NOAEL	18 months continuous	112 ppm	Inhalation exposure	No effects seen in gastro., hepatic, renal, or body wt. measures	Robertson et al., 1947
Fischer 334 Rat	Mortality	LD <sub>50</sub>	Single oral dose	22,800 mg/kg/d	oral	females	Clarke et al., 1979
Cat	Hematology (reticulocytosis, Heinz bodies, etc.)	LOAEL	14 d, in feed	36,000 mg/kg/d	oral		Weiss et al., 1992
CD-1 mouse	Reproduction	NOAEL	5 d; once/day	10,000 mg/kg/d	oral (gavage in water)		Kavlock et al., 1987
Cat	Decreased red blood cell survival	LOAEL	13 weeks, in feed	1,260 mg/kg/d	oral		Bauer et al., 1991
Cat (mongrel)	CNS depression, ataxia, decreased activity	LOAEL	22-35 d in feed	8,000 mg/kg/d	Oral		Christopher et al., 1990.
Swiss CD-1	Reproduction	NOAEL	15-18 wk daily,	10,018 mg/kg/d	Oral		NTP, 1985

Species	Effect	Endpoint	Exposure Duration	Reported Concentration	Methods	Notes	Reference
mouse			in water				
Swiss CD-1 mouse	Development	NOAEL	15-18 wk daily, in water	10,018 mg/kg/d	Oral		NTP, 1985
Rat	Respiratory Cardiac Hematological Hepatic Renal Endocrine	NOAEL	2 y, in food	2,500 mg/kg/d	Oral		Gaunt et al., 1972
Dog	Decreased erythrocytes, hematocrit, haemoglobin	LOAEL	2 y, in food	5,000 mg/kg/d	Oral		Weil et al., 1971
Dog	Immunological	NOAEL	2 y, in food	5,000 mg/kg/d	Oral		Weil et al., 1971
New Zealand Rabbit	Dermal	NOAEL	0.52 g applied to skin; once	0.52 g	Dermal		Clarke et al., 1979
Human	Neurological	LOAEL	70 h; >1 x/d	9,000 mg/kg	Dermal	Hypoxic encephalopathy	Fligner et al., 1985.
Human	Erythema	LOAEL	21-22 d	207 mg	Dermal	males	Trancik and Malbeck, 1982