Canadian Water Quality Guidelines for the Protection of Aquatic Life

GLYCOLS

ethylene glycol, propylene glycol, and diethylene glycol

Ethylene glycol (EG), 1,2-propylene glycol (1,2-PG), and diethylene glycol (DEG) are widely used in Canada as heat transfer fluids, automobile antifreeze, and polyester resins. Glycols are also the principal constituents of aircraft deicing/anti-icing fluids.

EG ($C_2H_6O_2$) is a nonvolatile (vapour pressure = 6.7 Pa at 20°C) colourless liquid that is miscible in water. Synonyms for EG include ethane-1-2-diol, ethylene alcohol, ethylene dihydrate, monoethylene glycol, glycol alcohol, 1,2-ethanediol, and 1,2-dihydroxyethane (Sax and Lewis 1989; Merck Index 1996). The CAS number for EG is 107-21-1.

In Canada, about 60% of EG consumed is used in aircraft deicing fluids and automobile cooling systems (CPI 1995). An additional 11% is used for the production of polyethylene terephthalate (i.e., polyester) (Chinn 1993). Minor uses include the processing of oil and gas and the production of solvents, explosives, cellulose film, and glycol esters (Chinn 1993; CIS 1994). Canadian production of ethylene glycols increased from 97 000 t in 1976 to 513 200 t in 1993. Industry expansion was expected to increase total ethylene glycol production capacity to 825 000 t by 1996 (CIS 1994). Approximately 70% of the ethylene glycol manufactured in Canada is exported to foreign markets. Only minor amounts are imported (CIS 1994).

1,2-PG ($C_3H_8O_2$) is a colourless liquid with a vapour pressure of 10.7 Pa (at 20°C); it is miscible in water. Common synonyms for 1,2-PG include 1,2-propanediol, methyl glycol, sirlene, trimethyl glycol, 1,2-dihydroxypropane, monopropylene glycol, and methyl-ethylene glycol (Sax and Lewis 1989; Merck Index 1996). The CAS number for 1,2-PG is 57-55-6.

In 1992, 17 100 t of 1,2-PG was consumed in Canada (Martin et al. 1994). In Canada, the largest single use of 1,2-PG is in the production of unsaturated polyester resins for fibreglass-reinforced polyester products. 1,2-PG is also used as a tobacco humectant, in cosmetic softeners, in food additives, and for miscellaneous uses, such as paint and antifreeze for recreational vehicles (CIS 1995). Although Canadian production of 1,2-PG ceased in 1993, demand continues to be met by imports (CIS 1995).

DEG ($C_4H_{10}O_3$) is also a nonvolatile (1.3 Pa at 20°C) colourless liquid that is miscible in water. DEG has been used in the petroleum industry as a natural gas dehydrator. DEG is also used in formulated aircraft deicing fluids. Common synonyms for DEG include 2,2′-oxy-bisethanol, diglycol, and 2,2′-oxydiethanol (Sax and Lewis 1989; Merck Index 1996). The CAS number for DEG is 111-46-6.

Gylcols enter aquatic environments through improper disposal of spent antifreeze, wastewater from production and use facilities, and transportation accidents (Zeitoun and McIlhenny 1971; Miller 1979). Data on glycol contamination of surface water are limited to sites near airports and are associated with aircraft deicing. Canadian airports have recently reported concentrations of EG from <1 to 2007 $mg \cdot L^{-1}$, PG from <1 to 890 $mg \cdot L^{-1}$, and DEG from <2 to 79 $mg \cdot L^{-1}$ (Transport Canada 1996). Total glycol levels in the effluents from Canadian airports ranged from <1 to 4105 $mg \cdot L^{-1}$ in 1994/95 (Transport Canada 1995).

Data on glycol residues in groundwater are limited to one Canadian airport. In 1985/86, the maximum reported concentration was 415 $mg \cdot L^{-1}$. The maximum DEG level was 188 $mg \cdot L^{-1}$. No concentrations of 1,2-PG >10 $mg \cdot L^{-1}$ were detected (Transport Canada 1985a, 1987).

Aerobic microbial biodegradation is the most important environmental fate process affecting glycols in surface waters. Aerobic biodegradation half-lives depend on temperature and range from <2 to 30 d, 2.5 to 30 d, and 3.5 to >20 d, for EG, 1,2-PG, and DEG, respectively (Price et al. 1974; Haines and Alexander 1975; Kaplan et al. 1982; Verschueren 1985; Williams 1995). Anaerobic metabolism of glycols is slower. For example, 100% of 1,2-PG degrades in 4 d under aerobic conditions, but in 9 d under anaerobic conditions. Anaerobic metabolism may release several relatively toxic transformation products such as acetaldehyde, ethanol, acetate, and

Table 1. Water quality guidelines for glycols for the protection of aquatic life (CCME 1997).[*]

Aquatic life	Guideline value ($mg \cdot L^{-1}$)		
	EG	1,2-PG	DEG
Freshwater	192[†]	500[†]	NRG[†]
Marine	NRG[‡]	NRG[‡]	NRG[‡]

[*]Note: The two caveats in the section Water Quality Guideline Derivation should be considered before applying these guidelines.
[†]Interim guideline.
[‡]No recommended guideline.

methane (Pearce and Heydeman 1980; Dwyer and Tiedje 1983; Schink and Stieb 1983).

The natural biodegradation of EG, 1,2-PG, and DEG may place high oxygen demands on aquatic ecosystems, causing ambient dissolved oxygen concentrations in receiving waters to fall below oxygen guideline values (Transport Canada 1985b, 1988; Sills and Blakeslee 1990). The extent of this effect depends on the quantity of glycols entering the environment and the physical, chemical, and biological conditions of the specific receiving site. Consequently, even at glycol levels below CCME guidelines, the oxygen level could drop below the recommended CCME guideline for dissolved oxygen (CCREM 1987, CCME 1997) and, therefore, pose a threat to aquatic organisms.

Glycols are miscible in water, therefore, they do not accumulate in aquatic biota (Miller 1979). Crayfish *(Procambarus* sp.*)* exposed to 50–1000 mg·L^{-1} EG for 61 d did not bioconcentrate significant amounts (Abdelghani et al. 1990).

Water Quality Guideline Derivation

The interim Canadian water quality guidelines for glycols for the protection of aquatic life were developed based on the CCME protocol (CCME 1991). It must be noted, however, that these guidelines may not protect against indirect effects of glycols on BOD or direct effects of formulated glycols, some of which are known to be more toxic than pure glycols. These factors should be considered during guideline implementation.

Freshwater Life

Acute toxicities (96-h LC_{50}) for fish range from 17.8 to 111 g·L^{-1} EG for rainbow trout *(Oncorhynchus mykiss)* and bluegill sunfish *(Lepomis macrochirus)*, respectively (Mayer and Ellersieck 1986). Chronic toxicity thresholds for fathead minnows *(Pimephales promelas)* fall between 22.5 and 51.9 g·L^{-1} (Beak Consultants 1995a; Pillard 1995). Invertebrates have a slightly lower toxicity range, with a 10-d IC_{25} of 2.6 g·L^{-1} for midges *(Chironomus tentans)* and a 96-h LC_{50} of 91.4 g·L^{-1} for crayfish *(Procambarus* sp.*)* (Abdelghani et al. 1990; Beak Consultants 1995a). The freshwater species most sensitive to EG is the green alga *Selenastrum capricornutum*, which has a 96-h LOEC for growth inhibition of 1923 mg·L^{-1} (Aéroports de Montréal and Analex Inc. 1994). An interim guideline for the protection of freshwater life for EG of 192 mg·L^{-1} was derived by multiplying the LOEC by a safety factor of 0.1 (CCME 1997).

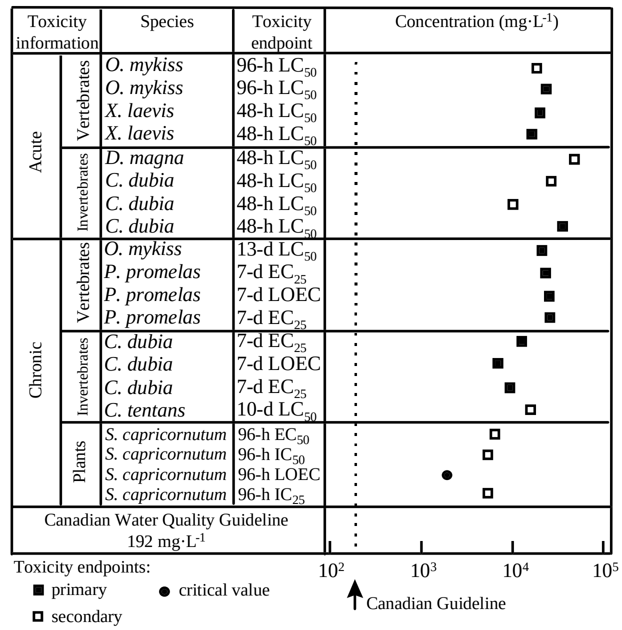

Figure 1. Select freshwater toxicity data for ethylene glycol.

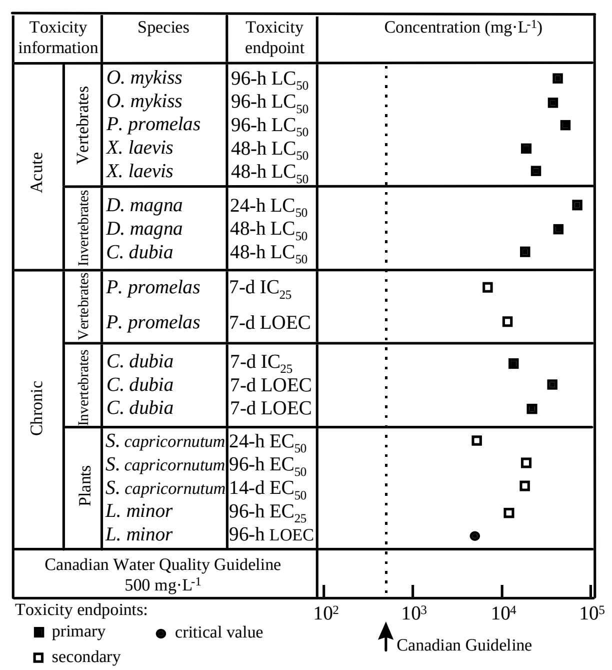

Figure 2. Select freshwater toxicity data for propylene glycol.

Acute toxicity thresholds of 1,2-PG for rainbow trout vary from 27.1 to 55.7 g·L^{-1} (Beak Consultants 1995b; Pillard 1995). The 7-d NOEC for growth and mortality of fathead minnows is 11.5 g·L^{-1} (Pillard 1995). Daphnids have similar tolerance limits, with a 7-d EC_{50} for impaired reproduction of 13.5 g·L^{-1} *(Ceriodaphnia dubia)* and a 24-h LC_{50} value of 70.7 g·L^{-1} (*Daphnia magna)* (Ward et al. 1992; Pillard 1995). The freshwater species most sensitive to 1,2-PG is duckweed *(Lemna minor)*, which has a 96-h LOEC for inhibition of frond growth of 5000 mg·L^{-1} (Dufresne and Pillard 1995). An interim guideline for the protection of freshwater life for 1,2-PG of 500 mg·L^{-1} was derived by multiplying the LOEC by a safety factor of 0.1 (CCME 1997).

Limited data on the acute toxicity of DEG to freshwater biota are available for fish, invertebrates, and algae. The freshwater species most sensitive to DEG is the green algae *S. capricornutum*, with a 24-h EC_{50} of 6400 mg·L^{-1} (Ward et al. 1992). The minimum data required for guideline development, however, do not exist (CCME 1991).

Marine life

Limited data on the acute toxicity of EG, 1,2-PG, and DEG to marine biota are available for fish, invertebrates, and algae. The marine species most sensitive to EG is the polychaete *Ophyrtrocha labronica*, which suffers 20% mortality following 40-d exposure to 55.7 mg·L^{-1} (Akesson 1970). The marine algae *Skeletonema costatum* is the most sensitive species to both 1,2-PG and DEG. The 14-d EC_{50} for 1,2-PG is <5.3 g·L^{-1}, and the 24-h EC_{50} for DEG is 8.9 g·L^{-1}. Water quality guidelines for the protection of marine biota were not developed for EG, 1,2-PG, or DEG at this time due to insufficient data (CCME 1991, 1997).

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