SOIL AND GROUNDWATER REMEDIATION GUIDELINES FOR DIETHYELENE GLYCOL AND TRIETHYLENE GLYCOL

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1. INTRODUCTION

Glycols are polyhydric alcohols, that is, aliphatic compounds with two or more hydroxyl (-OH) groups per molecule. Glycols have a wide range of uses including chemical feedstocks, solvents, and antifreeze. In addition, glycols are used in the dehydration of natural gas streams. Water in natural gas can cause operational problems in the transmission and processing of the gas (Sorensen et al., 2000), and thus gas dehydration units are ubiquitous at gas well sites and processing facilities. The most common dehydrating process used in the gas industry is the glycol absorption/stripping process (Katz and Lee, 1990). It is estimated that about 100,000 glycol dehydrating units exist worldwide (Grizzle, 1993).

The three glycols originally considered for soil and groundwater remediation guideline development were diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (TREG), which are formed by creating ether linkages between 2, 3, and 4 units of ethylene glycol (EG), respectively. Synonyms for these compounds are provided in Table 1. All three compounds have been used in glycol dehydration units. However, due to the lack of published toxicological information on TREG, and the fact that the use of this compound in glycol dehydration units is uncommon, only DEG and TEG were carried forward to the guideline development stage. The limited background data that were found concerning TREG are retained in this document for completeness.

For convenience, DEG, TEG, and TREG are collectively referred to in this document as "the Glycols". No soil or groundwater remediation guidelines have been published to date for any of the Glycols by either Alberta Environment (AENV) or the Canadian Council of Ministers of the Environment (CCME). This document develops proposed soil and groundwater remediation guidelines for DEG and TEG consistent with the Alberta Environment (AENV, 2009a) protocol.

Appendices A, B and C provide degradation and toxicological data specific to each of the three compounds, and include tables designated "Table A-1", "Table B-2", etc. Please refer to the appropriate appendices when reference is made to the corresponding table.

2. BACKGROUND INFORMATION

2.1 Chemical and Physical Properties

Chemical and physical properties of the Glycols are summarized in Table 2. The Glycols are polar organic compounds that are miscible with water. They have boiling points ranging from 245-314 °C and thus have negligible vapour pressures at typical environmental temperatures. The dimensionless Henry's law constant reported for TEG is 5.3×10^{-9} indicating that TEG will not volatilize when dissolved in water. DEG is assumed to have a dimensionless Henry's law constant close to zero. The negative log K_{oc} and K_{ow} values indicate that the Glycols would not be expected to be retarded in soil-groundwater systems or bioaccumulate in mammals.

2.2 Analytical Methods

One of the principal reference sources for analytical methods for water, soils, and other materials is the United States Environmental Protection Agency (U.S. EPA) Document SW-846: "*Test Methods for Evaluating Solid Wastes – Physical/Chemical Methods*" (U.S. EPA 2007d). The information below was summarized from this document.

One Alberta environmental laboratory analyzes glycols in soil samples using a modified version of U.S. EPA Method 3550A – "Ultrasonic Extraction", followed by U.S. EPA Method 8000A – "Determinative Chromatographic Separations". U.S. EPA (2007d) recommends method 8430 – "Analysis of bis(2-chloroethyl) ether and hydrolysis products by direct aqueous injection GC/FT-IR" for determination of EG and DEG.

Mrklas et al. (2003) developed a method for the analysis of TEG in water samples using ion exclusion chromatography with pulsed amperometric detection. Mrklas et al. (2004) used centrifugation to separate the supernatant prior to using the above technique on a soil/groundwater slurry.

2.3 Production and Uses

Major uses of DEG and TEG are shown in Figure 1.

Overview of Glycol Usage in Gas Dehydration

All three of the Glycols are used in natural gas dehydration. The following changes occur as the glycol chain length increases from DEG through TEG to TREG and are the main factors controlling the selection of the glycol compounds used in oilfield dehydration operations:

- increasing thermal stability;
- decreasing capacity for absorbing water; and,
- increasing cost.

DEG was commonly used for dehydration of natural gas prior to 1950 (Pearce, 1982), but is now used on relatively few units. Since 1950, TEG has been the most commonly used glycol for natural gas dehydration (Pearce, 1982). It has been estimated that TEG is currently used in 95% of glycol dehydration units (Thompson et al., 1993). TREG has the highest thermal stability and the lowest volatility of the glycols used for the dehydration of natural gas. However, because of its relatively high cost, it is generally used only in specialized cases (Sorensen et al., 1996). Small dehydration units are commonly located at wellsites, while larger glycol dehydrators may be present at natural gas processing plants.

The production and other uses of each of these compounds are discussed individually below.

DEG

DEG is a coproduct (9-10%) in the commercial synthesis of ethylene glycol by the hydrolysis of ethylene oxide. The quantity of co-product DEG produced exceeds demand for this chemical. DEG was first marketed by Union Carbide in 1928. The Dow Chemical Company remain a major supplier of this chemical. The global 1993 capacity for DEG production was estimated to be 359,000 ton/yr (Kirk-Othmer, 1999).

Major uses of DEG are summarized in Figure 1, and are as follows (Kirk-Othmer, 1999):

Natural Gas Dehydration	6%
Polyester Resins	45%
Antifreeze	14%
Manufacture of TEG	12%
Manufacture of Morpholine	10%
Miscellaneous [*]	13%

* Miscellaneous uses of DEG include plasticizers for paper, fiber finishes, compatibilizers for dye and printing ink components, latex paint antifreeze, and lubricants (Kirk-Othmer, 1999).

TEG

TEG is a minor coproduct in the commercial synthesis of ethylene glycol by the hydrolysis of ethylene oxide. However, the quantities produced in this process are not sufficient to satisfy demand, and additional TEG is produced by the reaction of ethylene oxide with DEG. The Dow Chemical Company is a major supplier of this chemical.

Major uses of TEG are summarized in Figure 1, and are as follows (Kirk-Othmer, 1999):

Natural Gas Dehydration	45%
Vinyl Plasticizer	13%
Solvent	11%
Manufacture of Ester Derivatives	12%
Miscellaneous	19%

TREG

TREG is produced by reacting lower molecular mass glycols (EG, DEG, TEG) with ethylene oxide. TREG is used in specialist natural gas dehydration applications. Although it is less hygroscopic than the lower members of the glycol series, it has a greater thermal stability. Other uses of TREG include a plasticizing agent for a variety of materials and an extraction solvent for benzene, toluene, and xylenes. No information was available on the relative amounts of TREG used in these various applications (Kirk-Othmer, 1999).

2.4 Sources and Emissions

Glycols in dehydrating units can potentially be released to the environment via spills, leaks, foaming events, or poor disposal of waste during changeover of units (Sorensen et al., 2000). Changeover refers to the process of replacing spent glycol with fresh, replacing filters, and cleaning/servicing the units. Glycols in gas dehydrating units are referred to as "raw", "rich", or "lean". Raw glycol refers to the fresh compound prior to use in a dehydrating unit. Rich glycol is glycol that has passed through the absorber and is enriched with water and possibly other polar chemicals from the gas stream. Lean glycol is glycol that has been regenerated in the boiler to remove the water and some of the other polar compounds.

A foaming event in a glycol-based dehydration unit is typically caused by the presence of hydrocarbons in the glycol stream, excessive use of additives, or high concentrations of degradation products (Sorensen et al., 2000). Foaming events can release a mixture of lean and rich glycols to the environment.

Changeover (periodic maintenance and cleaning) operations are also likely sources of fresh and spent glycols. The frequency of changeover operations varies from unit to unit and operator to operator, but they typically occur on a seasonal basis, though some units may go years between changeover events (Sorensen et al., 1996). The spent glycol solutions collected during the changeover process are typically managed by disposal into process waste pits. Historically, these pits may not have been lined. Leaking process waste pits have been the most common, and largest source of groundwater contamination at gas processing plants (Sorensen et al., 1996).

Leaks from dehydration units can occur, and may release significant amounts of rich or lean glycol into the environment, depending on the severity and duration of the leak. Catch basins may be placed under the valves and spigots at newer units to minimize the likelihood of leaks reaching the environment, but some older facilities may not use any management techniques (Sorensen et al., 1996).

Release of glycol to the atmosphere via regenerator off-gas is likely not a concern, based on the low vapour pressure of glycol (TEG has a vapour pressure of <1 mm Hg at 100 °C). However, note that the release of other compounds in the regenerator off-gas, particularly benzene, is a significant concern at some glycol dehydrator installations.

Glycol dehydration wastes may contain a number of co-contaminants, which are chemicals removed from the gas stream or glycol degradation products. Myerski et al. (1993) sampled spent glycols from storage tanks and dehydration units, and found that the concentrations of benzene in these waste streams can be as high as 110 mg/kg in TCLP¹ analysis. Sorensen et al. (2000) analyzed 29 samples of raw, rich, and lean glycols from gas processing facilities across north America, and found that rich glycols can contain relatively high levels of benzene, toluene, ethylbenzene and xylenes (BTEX), and potentially significant concentrations of naphthalene and other polycyclic aromatic hydrocarbons (PAHs). Lean glycols typically contained much lower concentrations of BTEX, and similar concentrations of naphthalene and other PAHs to rich glycols.

Glycols also have non-oilfield uses. The industrial uses (resins, plasticizers, manufacture of other chemicals) could potentially result in releases to the environment, but this is likely a concern only at a small number of facilities where these chemicals are manufactured or used for manufacturing other chemicals. Significant quantities of glycols can be used in aircraft de-icing operations. Aircraft de-icing fluids are typically composed primarily of ethylene glycol and/or propylene glycol, but may contain a small proportion of DEG (Sorensen et al., 1996).

2.5 Distribution in the Environment

No information was found that would indicate DEG, TEG, or TREG occur naturally in the environment. Accordingly, their distribution in the environment is expected to be strongly biased towards facilities where these compounds are produced or used. The number of facilities where the Glycols are used is significant. In the U.S., national surveys of occupational hazards were carried out in 1974 and 1983. The 1983 survey (NIOSH, 1983) indicated that the number of facilities where these glycols was used and the number of employees exposed to each was:

¹ Toxicity Characteristic Leaching Procedure (TCLP)

Glycol	Number of Facilities	Number of Employees Exposed
DEG	55,518	890,145
TEG	23,174	233,613
TREG	3,704	55,282

The physical and chemical properties of these glycols (Table 2) control the environmental media in which they are likely to be found. All three glycols have very low vapour pressures, and accordingly, their presence in the atmosphere will not be significant. All the Glycols could potentially be present in soil, groundwater, and/or surface water in the vicinity of facilities where they are used.

Glycol releases from oil and gas facilities can occur as a result of leaks from operating equipment, or through the improper disposal of wastes when glycol-using facilities are maintained.

Spills and releases of DEG, TEG, and TREG at gas plants are remediated where possible. In Alberta, frequency of spill reporting and concentrations of DEG are generally higher than TEG and TREG, with TREG typically having concentrations less than 10 mg/kg or non-detectable concentrations.

2.6 Human Exposure

Based on the physical and chemical properties of the Glycols, human exposure can occur via soil and water, but is not likely via the atmosphere, due to the negligible vapour pressure of the Glycols (Table 2). The potential, and very unusual, exception might be workers who could be chronically exposed to glycol fogging agents in theatre productions. Exposure via food and consumer products is possible for all the Glycols - the European Community have developed tolerable daily intakes for each of the Glycols to account for their possible presence in food-grade plastics, (European Commission, 2003). In addition, DEG is used in automobile antifreeze and brake fluids.

No regulatory estimates of the daily human exposure to the Glycols are available; therefore, in the absence of supporting information, the human estimated daily intake and the ambient air concentration and background soil concentration are assumed to be zero in areas isolated from facilities where the Glycols are used.

2.7 Existing Criteria, Guidelines and Standards

Only very limited information was found concerning guidelines, criteria, and standards for these chemicals.

Canadian Federal

CCME (1999 and updates) provides soil quality guidelines for ethylene glycol (960 mg/kg, based on the groundwater check for aquatic life). No CCME soil quality guidelines have been developed for DEG, TEG, or TREG. CCME (1999 and updates) provides water quality guidelines for the protection of freshwater aquatic life for ethylene glycol (192 mg/L) and propylene glycol (500 mg/L). Earlier CCME documents did have a water quality guideline for DEG, but this was rescinded in 1997, based on a lack of sufficient information. CCME water quality guidelines have not been developed for TEG or TREG.

Health Canada (2007) does not include any glycols in its "Guidelines for Canadian Drinking Water Quality". Health Canada (2004) does not publish Tolerable Daily Intakes for any glycols.

Canadian Provincial

The Ontario Ministry of Environment (OMEE, 1994) published an Interim Provincial Water Quality Objective (Interim PWQO) for DEG (11 mg/L). They also have PWQOs for EG, 1,2-propylene glycol and 1,3-propylene glycol. These Interim PWQOs are based on protection of all forms and life-stages of aquatic life for exposure over an extended period. No other provincial soil or water quality guidelines for DEG, TEG, or TREG were found.

US Federal

The U.S. EPA (2006, 2007c) does not publish a water quality guideline for DEG, TEG, or TREG protective of aquatic life, or Maximum Contaminant Levels (MCLs) for DEG, TEG, or TREG in drinking water. Neither DEG, TEG, nor TREG are included in the list of chemicals for which the U.S. EPA publishes Ecological Soil Screening Levels (EcoSSLs). No toxicological information is available on the U.S. EPA (2007a) IRIS database for DEG, TEG, or TREG.

US State

No criteria, guidelines, or standards were found in a limited search of U.S. state information.

Europe

The Dutch Ministry of the Environment (VROM, 2000) have published "Indicative Levels for Serious Contamination" for DEG (270 mg/kg in soil, and 13 mg/L in groundwater). VROM (2000) also included a DEG value for Human Maximum Permissible Risk (MPR) level of 0.4 mg/kg bw/day and an ecological HC50 of 480 mg/kg. HC50 is the hazardous concentration 50%, *i.e.*, the concentration at which 50% of the species and processes in an ecosystem are completely protected. VROM (2000) also have levels for EG, but not TEG, or TREG.

The United Kingdom Environment Agency develops Soil Guideline Values (SGVs) under its Contaminated Land Exposure Assessment (CLEA) program. Glycols have been identified for consideration, but no guidelines have been developed to date.

No other European guidelines for DEG, TEG, or TREG in soil or groundwater were found.

Australia and New Zealand

Australia and New Zealand have a collaborative set of water quality guidelines protective of aquatic uses (ANZECC, 2000). These guidelines do not include values for DEG, TEG, or TREG. No Australian drinking water guideline has been set for DEG, TEG, or TREG (NHMRC, 1996).

Global

The World Health Organization (WHO, 2004) does not include glycols in its "Guidelines for Drinking Water Quality, Third Edition".

Occupational Exposure Limits

The following occupational inhalation exposure limits for DEG are listed by NIOSH (2003):

Denmark:	time-weighted average 2.5 ppm (11 mg/m ³)
Poland:	MAC (time-weighted average) 10 mg/m ³
Russia:	short term exposure limit 10 mg/m ³
Sweden:	time-weighted average 10 ppm (45 mg/m ³) short term exposure limit 20 ppm (90 mg/m ³)
United Kingdom:	time-weighted average 23 ppm (101 mg/m ³)

3. ENVIRONMENTAL FATE AND BEHAVIOUR

3.1 Adsorption and Mobility

DEG and TEG have negative log K_{ow} (octanol-water partition coefficient) and log K_{oc} (organic carbon-water partition coefficient) values (Table 2), indicating that they partition to water in preference to a non-polar solvent or to soil organic carbon. Therefore, their mobility in the subsurface is unlikely to be limited by sorption to organic carbon.

No experimental data for the soil-water partition coefficient (K_d) of the Glycols were available. The Glycols are not significantly ionized at environmental pH values, as indicated by their high pKa values (14.5 for TEG, Table 2; 14.2 for EG; DEG assumed to be similar). Thus, interactions between ionized forms and charged clay surfaces can be ruled out. However, the Glycols are polar molecules and, as such, weak interactions with charged surfaces of clay minerals are expected. However, analytical techniques using an aqueous extraction appear to recover the Glycols quantitatively from soil samples, and thus it would appear that the binding of the Glycols to soils is minimal and the effective K_d of the Glycols is very small.

The values of K_d used in this document to assist in predicting the mobility of the Glycols in the subsurface were 9.0 x 10⁻⁵ L/kg for DEG and 2.6 x 10⁻⁵ L/kg for TEG, and were calculated by multiplying the Koc values in Table 3 by the assumed fraction of organic carbon in soil (0.005, Table 5).

3.2 Aqueous-Phase Solubility

The Glycols are all considered miscible with water (Table 2). Accordingly, the mobility of these compounds in the subsurface will not be limited by solubility.

3.3 Co-Solvency of Glycols and Hydrocarbons

Glycol dehydrators will remove lighter aromatic hydrocarbons (*e.g.*, BTEX, naphthalene, and their derivatives) from the gas stream where these compounds are present. Accordingly, releases of glycols to the environment may occur at the same location as releases of hydrocarbons. Sorensen et al. (2000) investigated the possible co-solvency of glycols and hydrocarbons, by investigating whether the addition of TEG could enhance the mobility of BTEX and naphthalene by reducing their soil/water partitioning coefficient (K_d). Their results varied with soil type and organic carbon content, but in several cases they were able to demonstrate a significant and sometimes dramatic reduction in the K_d values for BTEX, and particularly naphthalene, in the

presence of glycols. For example, the presence of a 40% solution of TEG reduced the K_d of naphthalene in an Alberta Till soil from 6.3 to <0.5 (units unspecified, but assumed to be L/kg).

3.4 Leaching and Lateral Movement

As noted above, the movement of the Glycols in the subsurface is not likely to be limited by either adsorption to organic carbon or solubility. The degree of sorption, if any, to clay minerals is not known. Consequently, leaching and lateral movement may be potentially significant factors in the subsurface transport of the Glycols.

3.5 Biodegradation

Although glycol releases at gas plants, airports, and other facilities are well documented, glycol plumes are not typically extensive in fine-grained Alberta soils, suggesting that biodegradation, and possibly other sorption and/or attenuation processes are active.

3.5.1 Degradation Pathways

Aerobic biodegradation of ethylene glycol has been suggested (e.g., Gonzalez et al., 1972; Caskey and Tabor, 1981) to occur via the pathway:

ethylene glycol \rightarrow glycollate \rightarrow glycylate \rightarrow tartronic semialdehyde \rightarrow glycerate.

However, none of the above degradation products are likely to be found in significant concentrations in the environment due to their rapid rates of degradation. Pearce and Heydeman (1980) indicate that acetaldehyde, ethanol, and acetate were observed as aerobic degradation products of ethylene glycol.

Anaerobic degradation of ethylene glycol has been shown to occur by several authors (e.g., Dwyer and Tiedje, 1983), though the rate is typically slower than for aerobic degradation. Most authors suggest the pathway :

```
ethylene glycol \rightarrow acetaldehyde \rightarrow ethanol \rightarrow acetate\rightarrow methane + CO<sub>2</sub>.
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Some or all of these compounds have been measured by various authors during anaerobic degradation.

The available literature (e.g., Sorensen et al., 1996) indicates that the most likely products of aerobic or anaerobic DEG or TEG degradation are acetaldehyde, ethanol, and acetate. The

pathway is assumed to be hydrolysis of the ether linkages followed by degradation of ethylene glycol by the pathways discussed above.

3.5.2 Inhibition of Biodegradation

TEG was reported to have no inhibiting effects on biodegradation at 4,000 mg/L (Verschueren, 2001). No inhibition data were available for DEG or TREG.

3.5.3 Degradation Rate

The AENV (2009a) model for remediation guidelines protective of freshwater aquatic life includes a parameter value for the degradation rate of the chemical in an aquifer. The discussion of glycol degradation rates provided below is focussed on determining a suitable value for this parameter.

Data on the degradation rate of the Glycols are provided in Tables A-1, B-1, and C-1 for DEG, TEG, and TREG, respectively. Data in these tables are categorized based on whether the studies used amendments (activated sludge, additional carbon source, nutrients, electron acceptors, etc.) or were unamended.

Many datapoints are available in the above-noted tables for studies conducted under amended conditions ("Other Studies" in Tables A-1 and B-1). For example, Haines and Alexander (1975) investigated the biodegradation of EG, DEG, TEG, and TREG under aerobic conditions in a slurry of a silt loam and nutrient solution (including phosphate), amended with bacterial cultures acclimated to polyethylene glycol degradation. Based on an indirect method using biological oxygen demand, they found that all four compounds degraded readily and completely in 5 days or less under these favourable conditions. Thus, it appears that, with suitable amendments, all three glycols can degrade rapidly (a few days to a few weeks) and completely.

However, in practice, degradation rates for many compounds in groundwater are limited by the availability of nutrients and/or electron acceptors. Accordingly, the degradation rates for studies conducted under amended conditions may have little relevance to likely degradation rates in an aquifer, and are not discussed further in this document. Studies with data from unamended, or potentially relevant conditions are discussed below.

Kaplan et al. (1982) investigated the biodegradation of DEG and TEG under aerobic, anaerobic, and abiotic (sterile) conditions. They found that both compounds degraded at similar rates in abiotic conditions, as in aerobic or anaerobic reactors, with or without the addition of nutrients or glucose. They concluded that degradation of these compounds was primarily abiotic. Data from this study were interpreted to give abiotic half lives of 20 days for DEG and 35 days for TEG. It

is noted that data from other studies do not support the relatively rapid abiotic degradation rates implied by Kaplan et al. (1982).

Mrklas et al. (2004) investigated the degradation of a mixture of monoethanolamine (MEA), EG, and TEG in slurries of contaminated soil and groundwater collected from a decommissioned sour gas plant. The study was designed with the objective of determining the potential for in-situ degradation of these compounds at the decommissioned sour gas plant. The initial level of TEG in the slurry was approximately 2,100 mg/kg. Aerobic and anaerobic studies were conducted on both biotic and abiotic bioreactors. TEG concentration was monitored directly using ion exclusion chromatography with pulsed amperometric detection. Biotic reactors received an addition of phosphate on day 11 or 64. Aerobic studies indicated that TEG degradation was limited by the availability of phosphate. Based on interpretation of data presented, in the absence of supplemental phosphate, the aerobic half life of TEG was much more rapid, with a half life of approximately 25 days. Anaerobic data presented in the paper could not be interpreted to yield an anaerobic degradation rate.

Sorensen et al. (2000) conducted an extensive series of aerobic and anaerobic biodegradation tests of TEG and DEG with three soils, one each from oil-producing areas of Alberta, New Mexico, and Louisiana. All experiments were conducted at 25° C at 60% moisture-holding capacity in the dark, and degradation progress was monitored indirectly by CO₂ production (respirometry). Initial concentrations of 200 mg/kg and 1,000 mg/kg glycol were monitored using wet chemistry respirometry. Other concentrations were monitored using electronic respirometry. However, the electronic respirometry data were inconsistent with the wet chemistry results, and are not discussed here. For TEG, the time for half of the glycol to be degraded based on CO₂ production in aerobic biometers ("pseudo-half life") ranged from 11 days to 131 days under aerobic conditions. For DEG, the pseudo-half life based on aerobic tests at 200 mg/kg and 1,000 mg/kg glycol ranged from 16 days to 250 days. It is noted that most of the soil microcosms showed a lag time before significant biodegradation commenced. Lag times varied from 1-6 days for the more biologically active soils under aerobic conditions.

Sorensen et al. (2000) also conducted studies under anaerobic conditions, but these studies are not included in Tables A-1 or B-1. Respirometry is not an appropriate method to use for anaerobic studies since carbon dioxide can be lost under methanogenic conditions as it is a potential electron acceptor. Thus, the Sorensen et al. (2000) anaerobic studies are not discussed further.

TEG

Overall, the most relevant degradation study was considered to be Mrklas et al. (2004), based on the following considerations:

- **Unamended**. The study showed that TEG degradation can be phosphate limited, and the first 64 days of some tests were conducted without the addition of phosphate or other amendments.
- **Direct Analysis**. TEG degradation was monitored by direct chemical analysis, rather than an indirect method such as respirometry.
- **Relevant Substrate.** The study was conducted with a slurry of soil and groundwater from a decommissioned sour gas plant in Alberta that had used TEG.
- **Relevant Concentration.** Initial TEG concentrations were relevant to conditions at a sour gas plant in Alberta; and,
- **Relevant Moisture Content.** Data from this study on a slurry is more relevant to aquifer conditions than data from studies on soils at typical soil moisture contents.

The TEG half life of 175 days interpreted from the unamended parts of tests in the Mrklas et al. (2004) study has been selected for use in the calculation of remediation guidelines.

DEG

Mrklas et al. (2004) does not include data for DEG. The abiotic degradation rates implied in the Kaplan et al. (1982) study are considered suspect as they are not supported by other studies. The most relevant of the remaining data are the aerobic results from the Sorensen et al. (2000) study. This study uses a relevant substrate and concentrations (soils from three oilfield areas including Alberta), and is unamended. However, the study uses an indirect method (respirometry) to determine degradation and is conducted at a moisture content relevant to unsaturated soils rather than an aquifer. Based on the above considerations, this study is more relevant to determining an appropriate degradation rate for use in the groundwater transport model than other available data.

The DEG half life used in this study in the calculation of remediation guidelines is 250 days, based on the longest of the half lives interpreted from six aerobic tests (Sorensen, 2000) with three soils at two concentrations (Table A-1). It is noted that the two tests conducted with Alberta soils both had DEG half lives shorter than this.

3.6 Volatilization

All three glycols have negligible vapour pressure at room temperature, and hence volatilization will not have a significant effect on the transport and fate of glycols in the subsurface.

3.7 Photodegradation

A photodegradation half life of 11.4 hours was calculated for TEG (Verschueren, 2001). No relevant information was found on the photodegradation of either DEG or TREG.

4. BEHAVIOUR AND EFFECTS IN AQUATIC BIOTA

Toxicological data for freshwater aquatic life for the Glycols were compiled from the U.S. EPA ECOTOX database (U.S. EPA, 2007b) and other sources. The studies have undergone classification into Primary, Secondary, or Unacceptable/unverified categories with respect to the CCME (2006) protocol. Based on the CCME protocol, only Primary and Secondary data are used to develop water quality guidelines.

Data gaps in the minimum dataset required to develop at least interim freshwater aquatic life guidelines were identified and an additional study was commissioned from Vizon SciTec Inc. to fill the gaps (Vizon, 2006).

4.1 DEG

Freshwater aquatic toxicity data for DEG are provided in Table A-2. Eighteen datapoints of Primary or Secondary quality from seven studies are included (Figure 2). Five datapoints are for vertebrates, three are for invertebrates, three for plants (green algae), and seven for other biota.

The studies which include Primary and Secondary quality data are discussed in more detail in Section 10.2.1.

An additional two datapoints of Unacceptable data quality were available. These were classified as Unacceptable based on a lack of sufficient information to confirm that controls were acceptable. Fourteen other datapoints that did not show an effect at the highest concentration(s) tested are also included in Table A-2 for completeness, but are not considered in the guideline development process.

4.2 TEG

Freshwater aquatic toxicity data for TEG are provided in Table B-2. Fifty one datapoints of Primary or Secondary quality from seven studies are included (Figure 2). Twenty four datapoints are for vertebrates, twenty six are for invertebrates, and one for other biota.

The studies which include Primary and Secondary quality data are discussed in more detail in Section 10.2.2.

An additional two datapoints of Unacceptable data quality were available. These were classified as Unacceptable based on a lack of sufficient information to confirm that controls were acceptable. Twenty nine other datapoints that did not show an effect at the highest concentration(s) tested are also included in Table A-2 for completeness, but are not considered in the guideline development process.

4.3 TREG

No Primary or Secondary data were available for TREG, and only one Unacceptable/unverified data point was found. This data point is included in Table C-2 for completeness but are not discussed further.

4.4 Marine Biota

Toxicological data for marine aquatic life for DEG, TEG, and TREG are provided in Table A-3, Table B-3, and Table C-3, respectively. A total of 4, 27, and 1 marine data point(s) were identified for DEG, TEG, and TREG, respectively. The papers reporting these data have not been reviewed in detail. The studies have undergone preliminary classification into Primary, Secondary, or Unacceptable/unverified categories with respect to CCME protocol. However, it is possible that some data classified as Secondary or Unacceptable would be upgraded based on a review of the original paper.

Marine toxicity data are included in this literature search for completeness, but are not directly relevant to developing soil or groundwater quality guidelines in Alberta and are not discussed further.

5. BEHAVIOUR AND EFFECTS IN TERRESTRIAL BIOTA

5.1 Terrestrial Plants

No data were found in the literature on the toxicity of DEG, TEG, or TREG to terrestrial plants. Accordingly, definitive (14 or 21 day) growth tests were commissioned (Stantec, 2006) to assess the toxicity of DEG and TEG to three plant species, alfalfa (*Medicago sativa*), barley (*Hordeum vulgare*), and northern wheatgrass (*Elymus lanceolatus*). Environment Canada (2005a) toxicity test protocols were used for this work with minor modifications as documented in Stantec (2006). A full report on these tests is available at <u>www.ptac.org</u>, and the results are summarized in Tables A-4 (DEG) and B-4 (TEG). EC25 values for various endpoints for these three species ranged from 419 mg/kg to 2,742 mg/kg (DEG) and 1,924 mg/kg to 10,953 mg/kg (TEG). TEG was the less toxic of the two glycols tested. These data are analyzed in more detail in Section 12.1.

5.2 Soil Invertebrates

No data were found in the literature on the toxicity of DEG, TEG, or TREG to terrestrial invertebrates. Accordingly, chronic survival and reproduction tests were commissioned (Stantec, 2006) for two invertebrate species, the earthworm *Eisenia andrei*, and the springtail *Folsomia canadida*. Environment Canada (2004, 2005b) toxicity test protocols were used for this work with minor modifications as documented in Stantec (2006). A full report on these tests is available at <u>www.ptac.org</u>, and the results are summarized in Tables A-5 (DEG) and B-5 (TEG). EC25 values for reproduction endpoints for these two invertebrates ranged from 4,842 mg/kg to 7,697 mg/kg (DEG) and 7,528 mg/kg to 13,701 mg/kg (TEG). TEG was the less toxic of the two glycols tested. These data are analyzed in more detail in Section 12.1.

5.3 Soil Microbial Processes

No data were found on the toxicity or effects of DEG, TEG, or TREG to soil microbial processes.

6. BEHAVIOUR AND EFFECTS IN HUMANS AND MAMMALIAN SPECIES

Mammalian toxicological data for DEG, TEG, and TREG are provided in Tables A-6, B-6, and C-4, respectively. General aspects of the toxicology of these glycols are summarized below, and key studies are discussed. Effect and no-effect levels for selected mammalian toxicological studies on DEG and TEG are provided in Figure 3, where circles show human data, diamonds show acute animal data, and triangles show chronic animal data. Hollow symbols indicate no effect levels and solid symbols indicate effects. Only toxicological data for oral administration are plotted in Figure 3.

Soviet Studies

A part of the toxicological database for these compounds comprises Soviet studies, mostly from the 1980s. In many cases, it is difficult to reconcile the results of these studies with the wider body of global literature. Frequently the toxic endpoints reported are different from those reported in all non-Soviet studies, or in other cases, the effect concentrations reported are inconsistent with the other studies. Anecdotally, some of the Soviet work from this period is reputed to be of poor quality, and was not carried out to the same standards (*e.g.*, good laboratory practice standards; OECD, 1998) as are used in reputable studies. There is not typically sufficient information available to confirm the standards to which these studies were carried out. Accordingly, the results of Soviet studies are not included in the discussion that follows or in Figure 3.

6.1 Absorption, Biotransformation, and Elimination

In general, relatively little information on the absorption, biotransformation and elimination of glycols was found. However, one more detailed paper on these processes in TEG was available, and accordingly, that compound is reviewed in a little more detail than DEG or TREG in the following discussion.

DEG

Little information was found concerning the absorption, biotransformation and elimination of DEG. Absorption of DEG through the skin of rats is slow; only 10% of the applied neat dose (open, but protected application) being absorbed over a 72 hour exposure (Mathews et al., 1991). Absorption of DEG following oral exposure is assumed to be relatively rapid and complete, based on its physical and chemical properties, and by analogy with TEG, but no studies confirming this were found. Winek et al. (1978) state that the metabolic pathway of DEG is largely unknown, but they consider it unlikely that DEG is metabolized to formate, and thus the acidosis characteristic of acute ethylene glycol (and methanol) poisoning is not expected to be a prominent feature of DEG intoxication.

TEG

Triethylene glycol appears to be readily absorbed following oral exposure, with the majority of the compound being eliminated in urine (either as the parent compound, or as a metabolite) within a 5 day period.

A detailed study by McKennis et al. (1962) looked at the absorption and excretion of 14 C radiolabelled and unlabelled TEG in rabbits and rats. At the end of a 5 day period, the total recovery of 14 C from rats was 91-89% of the administered dose. The majority (93-97% of the recovered dose) was recovered from the urine with a small amount (2-6% of the recovered dose) in feces and only a trace (0.8-1.2%) in exhaled air. Much of the urinary excretion of radioactivity appeared during the first 24 hours following administration.

McKennis et al. (1962) also investigated the metabolic degradation of TEG by analysis of the urine produced. A significant part of the administered dose was recovered (by chloroform extraction) as unchanged TEG (26-34% in the first 24 hours in rabbits; 27-66% in rats). Subsequent acidification and re-extraction of one sample of rabbit urine residue yielded a further 35% of the administered dose. The metabolite extracted was not identified, but postulated to be ethylene glycol with one or both terminal hydroxyl groups oxidized to carboxylic acid. The authors subjected the urine to acid hydrolysis and chloroform extraction but concluded that essentially none of the TEG was excreted as either an ether or ester derivative. They also found essentially no ¹⁴C activity in calcium oxalate precipitated from the urine samples, and concluded that the ether linkage was not broken during metabolism of TEG in rats. This is consistent with work by Schaffer et al. (1950) who studied the metabolism of polyethylene glycol was not a significant process for this compound. The authors used the lack of ¹⁴C in exhaled CO₂ to conclude that breaking of carbon-carbon linkages in TEG was not a significant metabolic pathway either. Lefaux (1968) confirmed that TEG is not metabolized to oxalic acid.

TREG

No information was found concerning the absorption, biotransformation, and elimination of TREG.

6.2 Acute Toxicity

DEG

The use of DEG in pharmaceuticals has caused the death of 71 adults in 3 separate incidents. Clinical findings included extensive kidney damage and less serious liver injury (BIBRA, 1993a). A similar range of acute symptoms has been reported in laboratory animals, where kidney and liver damage and central nervous system depression are the primary findings (BIBRA, 1993a). Oral LD50 values for laboratory animals range from 3,300 to 32,000 mg/kg bw (Table A-6). Most studies found DEG to be non-irritant by dermal exposure.

TEG

Limited information from animal studies reveal a range of acute toxic effects overlapping those for DEG (BIBRA, 1993b). Smyth et al. (1941) found that rats and guinea pigs fed TEG at doses approaching the LD50 appeared sluggish (possibly indicating depression of the central nervous system) and gross examination revealed kidney damage. Oral LD50 values for laboratory animals range from 8,800 to 22,000 mg/kg bw (Table B-6). Ocular and dermal studies found TEG to be non-irritant or mildly irritating.

TREG

For oral exposure, published values of the LD50 ranged from 1,875-34,000 mg/kg bw (Table C-4). Target organs identified were liver and kidney (BIBRA, 1993c). An ocular study found TREG to cause only minimal irritation.

6.3 Sub-Chronic and Chronic Toxicity

DEG

Key animal toxicity studies on the sub-chronic and chronic toxicity of DEG are discussed below.

In an unpublished study (BIBRA, 1976), groups of 15 rats of each sex were fed a diet containing 0.085, 0.17, 0.4 or 2% DEG for 255 days or 4% for 99 days. Slight effects on kidney function and urine composition were seen at 0.4% (300 mg/kg bw/day). The only possible effect seen in rats on the 0.17% diet (100 mg/kg bw/day, Lowest Observable Effect Concentration [LOEC]) was a marginal increase in urinary oxalate in male rats. No effects were noted at 0.085% (50 mg/kg bw/day, No Observable Effect Concentration [NOEC]).

Freundt and Weis (1989) reported that female rats receiving DEG at 200 mg/kg bw/day for 90 days in their water showed no effect on kidney weight or urine biochemistry.

No overt toxic effects were seen in mice maintained for 15-18 weeks on a diet providing a DEG dose of about 5,200 mg/kg bw/day (Morrissey et al., 1988). However, Huber et al. (1986) exposed mice to DEG in their drinking water for 14-17 weeks, and reported effects on blood clotting and immune response at DEG doses as low as 50 mg/kg bw/day.

The results of these and other studies are summarized in Table A-6 and Figure 3.

TEG

Fitzhugh and Nelson (1946) exposed male rats to 4% TEG in their diet (approximately 2,000 mg/kg bw/day) for 2 years. No effects on mortality, body weight, blood and urine composition, and gross and microscopic appearance of the major organs was reported.

Robertson et al. (1947) exposed rats to TEG in their drinking water at 3,000 mg/kg bw/day for 13 months. No effects on mortality, body weight, blood and urine composition, and gross and microscopic appearance of the major organs was reported.

Bossert et al. (1992) exposed mice to drinking water containing TEG for 14 weeks. No effects were seen at 3,300 mg/kg bw/day, but increased liver weight was observed at 6,800 mg/kg bw/day.

The results of these and other studies are summarized in Table B-6 and Figure 3.

TREG

The chronic and sub-chronic dataset for TREG is poor. The results of two Soviet studies are summarized in Table C-4.

6.4 Carcinogenicity and Genetic Toxicity

DEG

Available carcinogenicity and genotoxicity information for DEG is summarized in Table A-6.

DEG is not thought to be a primary chemical carcinogen. Bladder tumours in male rats fed high levels of DEG for long periods were seen only in animals with bladder stones. The data of Weil et al. (1965, 1967) support the contention that the tumours resulted from the chronic irritation of the stones on the bladder wall. DEG at levels below levels known to induce stone formation would therefore be unlikely to pose a carcinogenic risk to animals.

In-vivo tests on hamsters via intraperitoneal injection produced slight chromosomal damage; oral exposure produced equivocal results. *In-vitro* tests produced no point mutation or chromosomal damage with mammalian cells, and there was no evidence of mutagenicity in Ames tests using the bacterium *Salmonella typhimurium*.

Overall, the available data do not support either carcinogenicity or genotoxicity being significant concerns for DEG.

TEG

Available carcinogenicity and genotoxicity information for DEG is summarized in Table B-6.

No evidence of carcinogenicity was found in a 2 year study in which groups of 12 male rats received diets containing TEG at up to 2,000 mg/kg bw/day. Microscopic examinations were made of tissues from the major organs (Fitzhugh and Nelson, 1946).

The genotoxicity database for TEG is limited. Apart from some Soviet studies indicating various positive results, the only other information is an indication that TEG was genotoxic in an Ames bacterial test (no further details available, NTP, 1991).

Overall, the available data do not support either carcinogenicity or genotoxicity being significant concerns for TEG.

TREG

No human or animal data were found that were relevant in determining the status of TREG as a carcinogen.

Available genotoxicity information for TREG is summarized in Table C-4. No evidence of mutagenicity was seen in an Ames tests using the bacterium *Salmonella typhimurium*, or in mammalian cells in culture. There was an increase in chromosomal effects (sister chromatid exchange and damage) in mammalian cells, but the effect was weak and there was no dose-related trend. In mice given 5,000 mg/kg bw by intraperitoneal injection, chromosomal damage was induced in the peripheral blood cells, but rats given 5,000 mg/kg bw orally did not exhibit any increase of chromosomal damage in the bone marrow cells (BIBRA, 1993c).

Overall, the weight of available evidence does not suggest that genotoxicity is a significant concern for TREG. No direct evidence is available to assess the potential for carcinogenicity, however, analogy with DEG and TEG does not suggest that carcinogenicity is likely to be a significant concern for TREG.

6.5 Reproduction and Developmental Toxicity

DEG

Studies on the reproductive and developmental toxicity of DEG are summarized in Table A-6. The key studies are discussed briefly below.

The data for DEG indicate that developmental and reproductive endpoints are less sensitive than the effects seen in the chronic BIBRA (1976) study (NOEC = 50 mg/kg bw/day). Rodwell et al. (1987) found no effect on reproduction at 500 mg/kg bw/day when rats were exposed to DEG in drinking water continuously for 2 generations. Rodwell et al. (1987) found increased kidney weights in the parental and first generations at 1,500 mg/kg bw/day.

TEG

Studies on the reproductive and developmental toxicity of TEG are summarized in Table A-6. The key studies are discussed briefly below.

In a continuous breeding study, Bossert et al. (1992) exposed mice to TEG. Slightly reduced pup weight was noted at 3,400 mg/kg bw/day (LOEC), but no impairment of reproductive efficiency was noted in the first generation at 80 days. No effect on pup weight was noted at 680 mg/kg bw/day (NOEC).

Similar results were reported by U.S. EPA (1990), who found a NOEC of 600 mg/kg bw/day and a LOEC of 5,600 mg/kg bw/day for reduced fetal weight, reduced ossification, and increased skeletal variations when mice were exposed to TEG on day 6-15 of pregnancy.

Rats may be less sensitive than mice to reproductive and developmental effects of TEG, based on a 13 month continuous breeding study by Robertson et al. (1947), who found no overt effect on reproduction at 3,000 mg/kg bw/day.

TREG

There is little confidence in the quality of the small amount of available information on the reproductive toxicity of TREG (Table C-4).

6.6 Tolerable Daily Intake

Tolerable daily intake (TDI) is the daily oral dose of a contaminant that is assumed to be sufficiently low that humans could be exposed at this dose over an entire lifetime without adverse effects. The tolerable daily intakes identified for the Glycols are summarized below.

DEG

The European Community (EC)'s Scientific Committee on Food assigned a human TDI of 0.5 mg/kg bw/day for the intake of DEG (European Commission, 2008). This TDI is consistent with applying an uncertainty factor of 100 to the NOEC from the chronic BIBRA (1976) study, and is the value used in this document (Table 3).

TEG

The EC's Scientific Committee for Food (European Commission, 2003) assigned a TDI for man of 5 mg/kg bw/day for the combined intake of TEG and polyethylene glycol (European Commission, 2003). This TDI is consistent with applying an uncertainty factor of 100 to the NOEC from the Bossert et al. (1992) reproduction study, and rounding down, and is the value used in this document (Table 3).

TREG

The EC's Scientific Committee for Food assigned a TDI for man of 10 mg/kg bw/day for TREG (European Commission, 2003).

7. TOXICITY OF DEGRADATION PRODUCTS

In certain cases, organic compounds can have degradation products that are more toxic than the parent compound. Prudent management of such a parent compound should take into consideration the possibility of more toxic degradation products. A complete review of the toxicity of degradation products is outside the scope of the current study. However, it is worth noting that Sorensen et al. (1996) highlight formaldehyde, acetaldehyde, and ethanol as being potential glycol degradation products that are, or may be, more toxic than the parent compounds. Both formaldehyde and acetaldehyde are considered to be more toxic than DEG, with formaldehyde being the most toxic of these compounds. The Dutch environmental regulators (VROM, 2000), provide "indicative levels for serious contamination" for formaldehyde in soil and groundwater of 0.1 mg/kg and 0.05 mg/L, respectively. These values are 2-3 orders of magnitude lower than the corresponding values for DEG.

8. DATA ADEQUACY AND DATA GAPS

The available data were assessed against AENV (2009a) and CCME (2006) requirements for developing soil and water quality guidelines.

8.1 Soil Quality Guidelines

Human Health Guidelines

Sufficient data are available to develop soil quality guidelines protective of human soil ingestion, potable groundwater, and off-site migration. The indoor air inhalation guideline is not required, since the Glycols are not volatile. The guideline protective of ingestion of produce, milk and meat is not required, since the Glycols are not expected to biomagnify, based on their K_{ow} values.

Ecological Guidelines

None of the data available in the literature were suitable for calculating a soil contact guideline. A study was commissioned, which filled this data gap (Stantec, 2006).

None of the available data are suitable for calculating the nutrient and energy cycling check. A soil quality guideline can be calculated without this check.

Sufficient information was available to calculate a soil quality guideline protective of freshwater aquatic life, based on the surface water quality guideline for freshwater aquatic life discussed in Section 8.2.

Insufficient data exist to calculate the soil and food ingestion guideline. The CCME (2006) protocol for this guideline requires toxicity data from tests conducted on livestock species, and these data do not currently exist.

8.2 Water Quality Guidelines

Drinking Water

Sufficient data are available to develop Source Guidance Values for Groundwater based on the tolerable daily intake values discussed in Section 6.6.

Freshwater Aquatic Life

A study was commissioned (Vizon, 2006) to fill gaps in the freshwater aquatic life dataset. Including the new data from this study, there is sufficient information to develop interim freshwater aquatic life water quality guidelines for DEG and TEG. Insufficient data exist to develop a freshwater aquatic life water quality guideline for TREG.

Irrigation Water

Available data are currently insufficient to calculate an irrigation water guideline for any of the Glycols. In order to meet the CCME (1993) requirements to calculate this guideline for DEG and TEG, two additional toxicological studies would be required for each chemical, one on a cereal, tame hay, or pasture crop, and one on another crop.

Livestock Watering

Insufficient data are available to meet the requirements published in CCME (1993) for developing a livestock watering guideline.

9. PARAMETER VALUES

Parameter values required to calculate Alberta Tier 1 soil and groundwater remediation guidelines for DEG and TEG fall into two main groups: i) parameters that relate to the chemical properties, toxicity, or background exposure to the Glycols, referred to as "chemical-specific parameters"; and, ii) parameters relating to receptor exposure and properties of the site, referred to as "non-chemical-specific parameters". These two groups of parameters are discussed below.

9.1 Chemical-Specific Parameters

Chemical-specific parameters for DEG and TEG are summarized in Table 3, together with an indication of where to find a discussion of the rationale for the value selected. The soil allocation factor (SAF) and water allocation factor (WF) each take the values of 0.25, since exposure to DEG and TEG could reasonably be anticipated via four potentially contaminated environmental media: soil, water, food, and consumer products. However, exposure via air, the fifth potentially-contaminated medium, is unlikely due to the negligible vapour pressure of the Glycols (Section 2.6).

9.2 Non Chemical-Specific Parameters

Non chemical-specific parameter values are taken without change from AENV (2009a). Parameter values for human receptor characteristics, soil and hydrogeological parameters, site characteristics, and building parameters are provided in Tables 4 to 7, respectively.

10. SURFACE WATER GUIDELINES

AENV and the CCME use surface water quality guidelines as a basis from which to calculate corresponding groundwater and soil quality guidelines. Surface water quality guidelines calculated for DEG and TEG are provided and discussed below.

10.1 Human Drinking Water

No Canadian Drinking Water Quality Guideline (CDWQG) currently exists for any of the Glycols. In such cases, CCME (2006) includes a protocol for calculating an allowable concentration in potable water (Source Guidance Value for Groundwater) from the tolerable daily intake using the following equation:

$$SGVG = \frac{TDI \times BW \times WF}{WIR}$$

where:

SGVC		Source Guidance Value for Groundwater (mg/L)
TDI	=	tolerable daily intake (mg/kg/d)
BW	=	body weight (kg)
WF	=	water allocation factor (unitless)
WIR	=	water ingestion rate (L/d)

The SGVG is calculated using adult parameters (CCME, 2006). Substituting appropriate parameter values from Tables 3 and 4 gives values of 5.9 mg/L (DEG) and 59 mg/L (TEG). These values are rounded to 1 significant figure with a 5 or 0 in the second figure to give 6 mg/L (DEG) and 60 mg/L (TEG) which are the Source Guidance Values for Groundwater for these compounds (Table 8).

10.2 Freshwater Aquatic Life

Interim freshwater aquatic life water quality guidelines for DEG and TEG were calculated based on the CCME (1991) protocol. Freshwater aquatic toxicity data were obtained from the U.S. EPA ECOTOX database and other sources discussed in Section 4, and are summarized in Tables A-2 and B-2, for DEG and TEG, respectively.

Data Quantity Requirements

Insufficient data exist for the development of full freshwater aquatic life water quality guidelines for DEG or TEG. However, minimum data requirements are met for both chemicals for the development of an interim guideline (two acute and/or chronic studies on two or more fish

species, including one cold water species resident in North America; two acute and/or chronic studies on two or more invertebrate species from different classes, including one planktonic species). Thus, it was possible to develop interim freshwater aquatic life water quality guidelines for DEG and TEG.

Data Quality Screening

Wherever possible, all identified studies were identified and reviewed. In some cases, (e.g., foreign language journals and databases, data in books that are out of print) the original source could not be obtained, and it was necessary to rely on the ECOTOX reviewers for key study elements such as endpoints and acceptability of controls. Datapoints were assigned to Primary, Secondary, or Unacceptable categories, based on the CCME (1991) criteria. The most common reason for a study being categorized as Unacceptable was a lack of information indicating that controls were conducted and that control response was acceptable. Data where the concentration reported in the ECOTOX database was ">x" are included for completeness in a separate category in Tables A-2 and B-2. These data contain no information on concentrations at which effects are seen, and are not considered in the guideline development process. Where the ECOTOX database reported the same value for the same species and same author, this information is assumed to be redundant, and is only presented once in Tables A-2 and B-2.

Ecological Relevance

Guidelines are developed from ecologically relevant data. Accordingly, the toxicity endpoints in Tables A-2 and B-2 were screened for relevance to the ecological health of freshwater aquatic ecosystems.

10.2.1 DEG

The Primary and Secondary data for DEG included seven studies, details are summarized in Table A-2, and discussed below.

Bringmann and Kuhn (1980). This paper summarized the results of tests on 156 industrial pollutant chemicals on a bacterium (*Pseudomonas putida*), a green alga (*Scenedesmus quadricauda*), and a protozoan (*Entosyphon sulcatum*). All three species have been identified as being involved in the bioremediation of pollutant chemicals. These tests were evaluated to estimate the concentration of contaminant that would result in a 3% reduction in growth relative to controls (IC03) over the time period specified. The most sensitive of these species to DEG was *Scendesmus quadricauda*), with a 7 day IC03 of 2,700 mg/L. This test duration was considered chronic relative to typical unicellular algae cell proliferation rates.

de Zwart and Sloof (1987). This study was designed to investigate the toxicity of mixtures of chemicals, but also includes 48 hour LC50 values for 3-4 week old clawed toad larvae (*Xenopus*

laevis) exposed to 33 single chemicals including DEG. The 48 hour (acute) LC50 for this species for DEG was 3,065 mg/L.

Geiger et al. (1990). This book is a large compilation of acute toxicity data for the Fathead minnow, and is out of print. The Fathead minnow LC50 for DEG from the ECOTOX database reported in Table A-2 (75,200 mg/L) is broadly consistent with the Vizon (2006) LC50 for rainbow trout, and the Geiger et al. (1990) data are not limiting in the development of a DEG guideline. Accordingly, the original source was not reviewed for this datapoint.

Ward et al. (1992). A copy of this unpublished study was kindly provided for review by Environment Canada. Acute mortality studies were conducted on two freshwater fish (fathead minnow – *Pimephales promelas* and rainbow trout – *Oncorhynchus mykiss*), and one freshwater invertebrate (*Daphnia magna*). A chronic growth test was performed on the green alga *Selanastrum capricornutum*. Tests were also conducted on three marine species (Table A-3). Results for the animal species were consistent with other studies. Growth of *S. capricornutum* was measured at a range of time periods from 24 hours to 14 days, and appeared to indicate higher toxicity at earlier times. One possible reason for this could be the alga becoming acclimated to the toxicant. The concentration of DEG was relatively stable throughout the 14 day test, with the average measured concentration at 14 days being 79% of nominal. The 14 day result was considered to be the most relevant to the long-term health of an aquatic ecosystem, and accordingly the 14 day IC50 and LOEC are included in Table A-2.

Sauvant et al. (1995a,b). These two studies investigated the toxicity of a range of chemicals to *Tetrahymena pyriformis*. *T. pyriformis* is a ciliated protozoan (single-celled organism) found in freshwater bodies around the world. Accordingly, it is ecologically relevant to developing freshwater aquatic life water quality guidelines. The lowest reported LC50 value for the growth of this organism was 22,500 mg/L for a 36 hour test. All results in these studies are considered chronic, since the durations of the tests were long, compared with the doubling rate of 3 h for these protozoa.

Vizon (2006). This study is available at <u>www.ptac.org</u> and was commissioned to fill data gaps in the literature such that at least the minimum requirements for developing a CCME interim guideline were met. Vizon (2006) conducted 96 hour static lethality tests using rainbow trout and the freshwater amphipod *Hyalella azteca*, and a 48 hour static lethality test using *Daphnia magna*. Environment Canada biological test methods were used throughout (EPS 1/RM/9 for rainbow trout, EPS 1/RM/33 for *Hyalella azteca*, and EPS 1/RM/11 for Daphnia magna). All the requirements for Primary data quality were met, including measured chemical concentrations. Results are provided in Table A-2. The lowest acute LC50 was 63,000 mg/L, which was the 48 hour result for *D. magna*.

The CCME (1991) protocol for calculating the guideline considers Primary and Secondary data and takes the lower of:

- 1. the lowest LOEC for a chronic study for a non-lethal endpoint is multiplied by a safety factor of 0.1.
- 2. The lowest EC50 or LC50 for an acute test is multiplied by an application factor of 0.05 (DEG is considered non-persistent in surface water based on the degradation data provided in Table A-1 for conditions where oxygen and nutrients are not limiting).

Chronic Studies

The lowest endpoint from a chronic study among the Primary and Secondary data in Table A-2 is 2,700 mg/L, which is the Bringmann and Kuhn (1980) IC03 for growth inhibition in the green alga *Scenedesmus quadricauda*. Therefore, a freshwater aquatic life water quality guideline based on a chronic study is calculated by multiplying the IC03 of 2,700 mg/L from this study by a safety factor of 0.1 to give a guideline value of 270 mg/L.

Acute Studies

The freshwater guideline derived from the lowest relevant acute EC50/LC50 is calculated by multiplying the de Zwart and Sloof (1987) 48 hour LC50 for the clawed toad *Xenopus laevis* (3,065 mg/L) by an application factor of 0.05 (non-persistent variable) to give a guideline value of 153 mg/L.

The guideline value from the acute study is the lower of the two values calculated above, and accordingly, the freshwater aquatic life water quality guideline for DEG is 153 mg/L. This value is rounded to 1 significant figure with a 5 or 0 in the second figure to give 150 mg/L (Table 8).

10.2.2 TEG

Many of the studies on the freshwater aquatic toxicity of TEG were conducted to assess the potential effects of TEG when used as a solvent in toxicity tests of lipophilic chemicals ("carrier solvent"). The Primary and Secondary data in Table B-2 include the following eight studies, discussed below.

Cardwell et al. (1978). A copy of this unpublished study was kindly provided for review by the Mid-Continent Ecology Division of the U.S. EPA in Duluth, Minnesota. This detailed report provided information on a study that was undertaken to investigate the acute and chronic toxicity of TEG and 3 other carrier solvents to fathead minnow (*Pimephales promelas*), brook trout (*Salvelinus fontinalis* Mitchill), and bluegill (*Lepomis macrochirus* Rafinesque). The summary data on this study included in the U.S. EPA (2007b) ECOTOX report contain some inaccuracies

relative to the content of the report, and Table B-2 reflects the source report rather than the ECOTOX summary.

- *Acute Tests*. Acute lethality tests were conducted in flow-though aquaria for all three species with test durations ranging from 12 h to 7 days (168 hours). Static acute tests were also conducted with fathead minnows only. Results are summarized in Table B-2. The most sensitive species was the bluegill, and the lowest acute LC50 was the 7 day result for bluegill, 60,157 mg/L.
- *Chronic Tests*. Significant resources were expended in conducting two generation chronic tests with brook trout (15 months total duration) and fathead minnow (12 months total duration). A wide range of endpoints were considered in each test, including hatching success, mortality, length, weight and spawning success of the F₀ generation, and hatching success, mortality, length, and weight of the F₁ generation. No significant effect was seen on the growth (length or weight) of either the F₀ or the F₁ generations. Unfortunately, utility of the results from these tests was compromised by the following factors:
 - The study design did not have adequate power to determine statistical significance for many of the endpoints.
 - Maximum test concentrations were not high enough to determine effect levels for many of the endpoints considered.
 - On two instances, inadvertent chlorination of the supply water caused significant mortality of the brook trout alevins, and compromised the data from that test.
 - Some fish were damaged by handling and/or fighting during the tests, and developed infections of the fungus *Saprolegnia parasitica*. Either the fungus or the attempted treatment proved fatal to these fish.
 - Several fish developed apparent bacterial hemorrhagic septicemia, which was treated by the antibiotic oxytetracycline, adding further uncertainty to the test results.
 - All aquaria became contaminated with a bacterium believed to be *Sphaerotilus* sp. which proliferated to such an extent that twice weekly cleaning of aquaria was required. In the higher concentration treatments, bacterial growth was observed on the surface of the eggs, which was postulated by the authors to reduce the availability of oxygen to the eggs and potentially be a cause of the increased number of abnormal fry at hatch seen in some treatments.

Overall, the data from the Cardwell et al. (1978) chronic tests were considered to be irrevocably compromised by the factors noted above, and the data are not included in Table B-2 or considered further in the development of a water quality guideline.

Bringmann and Kuhn (1978). This study was not obtained for review (foreign language journal), however, based on the data reported in the ECOTOX database and extrapolation from other similar work conducted by these authors, it is likely that acceptable controls were included. The study investigated the toxicity of TEG to the blue-green alga *Microcystis aeruginosa*. Since it appears that algae are some of the most sensitive organisms to glycols, the precautionary principle dictates that the results of this study should be taken at face value. Two other studies by the same authors reported the same value for another species of blue-green alga. The study reported a LOEC for 8 day *Microcystis aeruginosa* growth of 3,600 mg/L. This duration is considered chronic for algae.

Barera and Adams (1983). This study examined various aspects of the American Society for Testing and Materials (ASTM) standard for conducting acute toxicity tests with Daphnia magna, including the use of carrier solvents such as TEG. Based on the information provided in the paper, the study appears to be of high quality in all respects including the reporting of controls. Chemical concentrations were nominal, rather than measured, and accordingly, the study is designated of Secondary data quality. The study reports a 24 hour LC50 of 88,500 mg/L, a 48 hour LC50 of 52,400 mg/L, and a 48 hour mortality NOEC of 24,000 mg/L.

LeBlanc and Surprenant (1983). This study was designed to validate the use of 3 carrier solvents including TEG in toxicity tests with *Daphnia magna*. Based on the information provided in the paper, the study appears to be of high quality in all respects including the reporting of controls. Chemical concentrations were nominal, rather than measured, and accordingly, the study is designated of Secondary data quality. Acute mortality tests were conducted in static test vessels, and yielded a 24 hour LC50 of 58,000 uL/L (65,250 mg/L) and a 48 hour LC50 of 35,000 uL/L (39,375 mg/L). Chronic 28 day survival and reproduction tests were conducted in flow-through aquaria, and a LOEC of 11,000 uL/L (12,375 mg/L) was determined for both survival and reproduction.

Adams and Heidolph (1985). This study was designed to develop application factors used to extrapolate the results of *Daphnia magna* acute or partial life-cycle tests to the anticipated result for a 21 day geometric mean maximum acceptable toxicant concentration (GM-MATC). This large study examined eight test chemicals including TEG. Based on the information provided in the paper, the study appears to be of high quality in all respects including the reporting of controls. Chemical concentrations were nominal, rather than measured, and accordingly, the study is designated of Secondary data quality. Acute mortality tests (24 and 48 hour) were conducted in static test vessels. Results from acute tests appear to be the same data as reported by Barera and Adams (1983). Chronic tests considered growth, survival and reproduction at 7, 14, and 21 days and were conducted under renewal conditions. Results are provided in Table B-2. The lowest acute LC50 in this study was 42,426 mg/L (measured at day 2 of the chronic test). The lowest chronic LOEC was 15,000 mg/L for *D. magna* growth at 21 days.

Ziegenfuss et al. (1986). This study was designed to investigate the effect of water-sediment partitioning on the toxicity of a range of chemicals, including TEG, on one benthic invertebrate (*Chironomus tentans*) and one free-swimming invertebrate (*Daphnia magna*). Toxicity data were also included for standard acute toxicity tests (without sediment).

Geiger et al. (1990). This book is a large compilation of acute toxicity data for the fathead minnow, and is out of print. The data for TEG from the ECOTOX database reported in Table B-2 are broadly consistent with the other fish toxicity data for this chemical, and the original source for these data was not reviewed.

Vizon (2006). This study is available at <u>www.ptac.org</u> and was commissioned to fill data gaps in the literature such that at least the minimum requirements for developing a CCME interim guideline were met. Vizon (2006) conducted a 96 hour static lethality test using the freshwater amphipod *Hyalella azteca*. Environment Canada biological test method EPS 1/RM/33 was used and all the requirements for Primary data quality were met, including measured chemical concentrations. The 48 hour LC50 was 43,500 mg/L, essentially consistent with the data for *D. magna* determined in other studies.

The CCME (1991) protocol for calculating the guideline considers Primary and Secondary data and takes the lower of:

- 1. the lowest LOEC for a chronic study for a non-lethal endpoint is multiplied by a safety factor of 0.1.
- 2. The lowest EC50 or LC50 for an acute test is multiplied by an application factor of 0.05 (TEG is considered non-persistent in surface water based on the degradation data provided in Table B-1 for conditions where oxygen and nutrients are not limiting).

Chronic Studies

The lowest endpoint from a chronic study among the Primary and Secondary data in Table B-2 is 3,600 mg/L which is the 8 day LOEC for *Microcystis aeruginosa* growth in the Bringmann and Kuhn (1978) study. Therefore, a freshwater aquatic life water quality guideline based on a chronic study is calculated by multiplying the LOEC of 3,600 mg/L from this study by a safety factor of 0.1 to give a guideline value of 360 mg/L.

Acute Studies

The lowest endpoint from an acute study among the Primary and Secondary data in Table B-2 is 39,375 mg/L which is the 48 hour LC50 for *Daphnia magna* mortality in the LeBlanc and Surprenant (1983) study. The freshwater guideline derived from the lowest relevant acute LC50

is calculated by multiplying this value by an application factor of 0.05 (non-persistent variable) to give a guideline value of 1,969 mg/L.

The guideline from the chronic study is the lower of the two guidelines calculated, and accordingly, the freshwater aquatic life water quality guideline for TEG is 360 mg/L. This value is rounded to 1 significant figure with a 5 or 0 in the second figure to give 350 mg/L (Table 8).

10.3 Irrigation Water

No guideline was calculated for the Glycols in irrigation water since the minimum data requirements were not met (Section 8.2).

10.4 Livestock and Wildlife Watering

Toxicity data for the Glycols were not available for livestock or wildlife species (Section 8.2), and accordingly, these guidelines could not be calculated.

11. SOIL AND GROUNDWATER GUIDELINE CALCULATIONS - HUMAN HEALTH

11.1 Direct Contact

The model used to calculate the soil quality guideline protective of the human direct soil contact (soil ingestion, dermal contact, and particulate inhalation) exposure pathway for the Glycols is taken without change from AENV (2009a). Parameter values are summarized in Tables 3 and 4. The following equation was used.

$$PSQG_{HH} = \frac{(TDI - EDI) \times SAF \times BW}{\left[\left(AF_G \times SIR \right) + \left(AF_L \times IR_S \times ET_2 \right) + \left(AF_S \times SR \right) \right] \times ET_1} + \left[BSC \right]$$

Where:

PSQG _{HH}	=	preliminary human health-based soil quality guideline (mg/kg)
TDI	=	tolerable daily intake (mg/kg bw per day)
EDI	=	estimated daily intake (mg/kg bw per day)
SAF	=	soil allocation factor (dimensionless)
BW	=	adult or toddler body weight (kg)
AF _G	=	absorption factor for gut (dimensionless)
AF_L	=	absorption factor for lung (dimensionless)
AFs	=	absorption factor for skin (dimensionless)
SIR	=	adult or toddler soil ingestion rate (kg/day)
IR _s	=	inhalation of particulate matter re-suspended from soil (kg/day)
SR	=	adult or toddler soil dermal contact rate, see below (kg/day)
ET_1	=	exposure term 1 (dimensionless) (days/week ÷ 7 x weeks/year ÷ 52)
ET_2	=	exposure term 2 (dimensionless) (hours/day ÷ 24)
BSC	=	background soil concentration (mg/kg)

Substituting appropriate values from Tables 3 and 4 into this equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives human direct contact guideline values of:

DEG (Tables 9 and 10):

- 15,000 mg/kg (agricultural and residential);
- 20,000 mg/kg (commercial); and,
- 100,000 mg/kg (industrial).

TEG (Tables 11 and 12):

- 150,000 mg/kg (agricultural and residential); and,
- 200,000 mg/kg (commercial).

• no guideline is required ("ngr" in Tables 11 and 12) for industrial land use since the calculated value is $>10^6$ mg/kg.

Soil Dermal Contact Rate

The soil dermal contact rate (SR) is the mass of contaminated soil which is assumed to contact the skin each day. This parameter is calculated as follows (AENV, 2009a):

$$SR = \{(SA_H \times DL_H) + (SA_O \times DL_O)\} \times EF$$

Where:

SR	=	soil dermal contact rate (kg/day)
SA_H	=	exposed surface area of hands (m ²)
DL_H	=	dermal loading of soil to hands (kg/m ² per event)
SA ₀	=	area of exposed body surfaces other than hands (m ²)
DLo	=	dermal loading of soil to other surfaces (kg/m ² per event)
EF	=	exposure frequency (events/day)

The soil dermal contact rate is calculated separately for toddlers and adults using the parameters in Table 4, and is 6.88×10^{-5} kg/day for toddlers, and 1.14×10^{-4} kg/day for adults.

11.2 Inhalation

The Glycols are effectively non-volatile (Section 3.6) and accordingly remediation guidelines protective of the indoor air inhalation exposure pathway are not calculated for either soil or groundwater.

11.3 Offsite Migration

Offsite Migration guidelines are calculated to check that the guidelines set for commercial and industrial land use will not result in adjacent more sensitive land being contaminated at levels above the applicable guideline for the sensitive land due to wind and/or water transport of contaminated soil from the commercial or industrial site. The human health offsite migration guideline is calculated using the equation provided in AENV (2009a):

$$SQG_{OM} = (14.3 \times SQG_A) - (13.3 \times BSC)$$

Where

SQG_{OM}= soil quality guideline protective of offsite migration (mg/kg) SQG_A = soil quality guideline for human direct soil contact for agricultural land use (mg/kg) BSC = background soil concentration (mg/kg)

Substituting appropriate values from Tables 3, 9, 10, 11, and 12 into this equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives a human health offsite migration guideline of 200,000 mg/kg for DEG; Tables 9 and 10. No guideline is required ("ngr" in Tables 11 and 12) for TEG since the calculated value is $>10^6$ mg/kg.

12. SOIL AND GROUNDWATER GUIDELINE CALCULATIONS - ECOLOGICAL

12.1 Direct Contact

12.1.1 Soil

The soil quality guideline for the exposure pathway considering direct contact of plants and soil invertebrates (the "eco-contact pathway") was calculated for DEG and TEG based on a weight of evidence approach following CCME (2006). Data relevant for guideline development are sourced from Stantec (2006) (available at <u>www.ptac.org</u>) and are summarized in Tables A-4 and A-5 (DEG) and B-4 and B-5 (TEG). The values provided in the above-noted tables are nominal values based on the known amount of chemical spiked into the test soils. Stantec (2006) included analytical data to confirm exposure concentrations. Analytical data from day 0 in the definitive tests were analyzed to give the following regressions:

y = 1.0184x - 220.28 (DEG)

y = 1.0145x - 256.93 (TEG)

where x is the nominal concentration and y the measured concentration.

		I	C25
		(Corrected for A	nalytical Recovery)
Species	Effect	DEG	TEG
		(mg/kg)	(mg/kg)
Alfalfa	Shoot Length	1,101	7,005
Alfalfa	Root Length	1,296	9,543
Alfalfa	Shoot Dry Mass	2,359	6,454
Alfalfa	Root Dry Mass	2,297	7,284
Barley	Shoot Length	2,536	7,530
Barley	Root Length	2,572	10,855
Barley	Shoot Dry Mass	206	4,120
Barley	Root Dry Mass	766	4,949
Northern Wheatgrass	Shoot Length	1,552	4,887
Northern Wheatgrass	Root Length	1,703	5,533
Northern Wheatgrass	Shoot Dry Mass	613	1,695
Northern Wheatgrass	Root Dry Mass	919	1,915
Eisenia andrei	Number of Progeny	7,618	9,298
Eisenia andrei	Dry Mass of Individual Progeny	4,711	7,380
Folsomia candida	Number of Progeny	5,219	13,643

These regressions indicate essentially quantitative recovery of these glycols from the test soils. The CCME (2006) protocol uses data standardized at the 25th percentile effect level. Invertebrate survival data were not calculated at the 25% effect level by Stantec (2006), and were not included in the calculation of guideline values. The data that were used to calculate the eco-contact guideline are presented below. These data have been corrected for analytical recovery from the values in Tables A-4, A-5, B-4, and B-5.

The 25th percentile of these data is the eco-contact guideline for natural areas, agricultural, and residential. The 50th percentile of these data is the eco-contact guideline for commercial and industrial land use. The eco-contact guidelines for DEG and TEG are summarized below (rounded to 1 significant figure with a 5 or a 0 as the second figure) and included in Tables 9, 10, 11, and 12.

DEG

- 25th percentile natural areas, agricultural, and residential: 1,000 mg/kg.
- 50th percentile commercial and industrial: 1,500 mg/kg.

TEG

- 25th percentile natural areas, agricultural, and residential: 5,000 mg/kg.
- 50th percentile commercial and industrial: 7,000 mg/kg.

12.1.2 Groundwater

The direct contact of shallow groundwater with plants and soil invertebrates exposure pathway is applicable whenever groundwater is present within 3 m of the ground surface. However, based on guidance in AENV (2009a), the guideline is not calculated for polar compounds such as the Glycols. The rationale for this position is that the potential interactions between polar organic compounds and soils are complex in that they can be highly dependant on various environmental conditions including pH, clay mineralogy, and redox conditions. Attempting to set groundwater guidelines for polar chemicals for this pathway would involve significant uncertainty, and accordingly, it is recommended that concerns with potential adverse effects on surface soil biota from polar organic compounds in shallow groundwater be addressed on a site-specific basis by analyzing soil samples.

Accordingly, the groundwater guideline protective of the eco-contact pathway is not calculated for the Glycols.

12.2 Nutrient and Energy Cycling

Insufficient data were available and this guideline was not calculated for the Glycols.

12.3 Soil and Food Ingestion

Insufficient data were available (Section 8.1), and this guideline was not calculated for the Glycols. However, this exposure pathway was not expected to be a concern, since i) the Glycols are expected to degrade rapidly in surficial soil (Section 3.5) and accordingly livestock and wildlife are unlikely to get significant exposure to the Glycols through incidental ingestion of surficial soil; and ii) based on their very low K_{ow} values (negative log K_{ow} ; Table 2) DEG and TEG are not expected to accumulate into plants to any significant extent; thus, the exposure of livestock or wildlife to DEG and TEG in soil via ingestion of fodder is expected to be minimal.

12.4 Offsite Migration

Offsite Migration guidelines are calculated to check that the guidelines set for commercial and industrial land use will not result in adjacent more sensitive land being contaminated at levels above the applicable guideline for the sensitive land due to wind and/or water transport of contaminated soil from the commercial or industrial site. The ecological offsite migration guideline is calculated using the equation provided in AENV (2009a):

$$SQG_{OM} = (14.3 \times SQG_A) - (13.3 \times BSC)$$

Where SQG_{OM}= soil quality guideline protective of offsite migration (mg/kg) SQG_A = soil quality guideline for ecological direct soil contact for agricultural land use (mg/kg) BSC = background soil concentration (mg/kg)

Substituting appropriate values from Tables 3, 9, 10, 11, and 12 into this equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives ecological offsite migration guidelines of 15,000 mg/kg for DEG (Tables 9 and 10), and 70,000 mg/kg for TEG (Tables 11 and 12).

13. SOIL AND GROUNDWATER GUIDELINE CALCULATIONS – GROUNDWATER PATHWAYS

This section provides the protocols used to calculate soil and groundwater remediation objectives protective of exposure pathways involving groundwater. The following receptors are considered:

- humans (potable drinking water sourced from groundwater); and,
- aquatic life (via lateral groundwater transport and discharge into a surface water body).

In the first case, it is assumed that a water well could potentially be installed at any location, and hence it is assumed that there is no lateral offset between the location where the contaminated soil or groundwater is measured and the receptor.

In the second case, a minimum lateral separation of 10 m is assumed between the location where the contaminated soil or groundwater is measured and the location of the surface water body. In cases where contamination is present within 10 m of a surface water body, a site-specific approach will be required (see AENV, 2009b).

Surface water quality guidelines protective of the above water uses are provided in Table 8. As noted in Section 10, insufficient data are available to calculate surface water guidelines for the Glycols protective of irrigation, wildlife or livestock watering, and accordingly, neither soil nor groundwater guidelines protective of these water uses could be calculated.

13.1 Soil Remediation Guidelines

Soil remediation guidelines for groundwater pathways were calculated using the model and equations from AENV (2009a)

13.1.1 Model Assumptions

Assumptions implicit in the model include the following:

- the soil is physically and chemically homogeneous;
- moisture content is uniform throughout the unsaturated zone;
- infiltration rate is uniform throughout the unsaturated zone;
- decay of the contaminant source is not considered (*i.e.*, infinite source mass);
- contaminant is not present as a free phase product;
- maximum possible concentration in the leachate is equivalent to the solubility limit of the chemical in water under the defined site conditions;

- the groundwater aquifer is unconfined;
- groundwater flow is uniform and steady;
- co-solubility and oxidation/reduction effects are not considered;
- attenuation of the contaminant in the saturated zone is assumed to be one dimensional with respect to sorption-desorption, dispersion, and biological degradation;
- dispersion in groundwater is assumed to occur in the longitudinal and transverse directions only and diffusion is not considered;
- mixing of the leachate with the groundwater is assumed to occur through mixing of leachate and groundwater mass fluxes; and
- dilution of the plume by groundwater recharge down-gradient of the source is not considered.

13.1.2 Guideline Calculation

The soil remediation guideline protective of groundwater uses is calculated in the same way for both groundwater uses noted at the start of this section, using the corresponding surface water quality guideline (Table 8) as the starting point for each. However, as noted above, the lateral offset between the point at which the contaminated soil is measured and the surface water body (parameter "x" in the equation for DF4 below) is assumed to be 10 m for aquatic life, and 0 m for human drinking water.

The model considers four processes:

- 1. partitioning from soil to leachate;
- 2. transport of leachate from base of contamination to water table;
- 3. mixing of leachate and groundwater; and,
- 4. groundwater transport down-gradient to a discharge point.

For each of these four processes, a dilution factor was calculated (DF1 through DF4, respectively). DF1 has units of (mg/kg)/(mg/L) or L/kg. The other three dilution factors are dimensionless [units of (mg/L)/(mg/L)]. The overall dilution factor is used to calculate the soil concentration that is protective of groundwater using the following equations:

$$SQG_{GR} = SWQG \times DF$$

$$DF = DF1 \times DF2 \times DF3 \times DF4$$

where: SQG_{GR}= soil quality guideline protective of groundwater pathways (mg/kg) SWQG= corresponding surface water quality guideline (drinking water or aquatic life) (mg/L)

DF	=	overall dilution factor (L/kg)
DF1	=	dilution factor for process 1 (L/kg)
DF2	=	dilution factor for process 2 (dimensionless)
DF3	=	dilution factor for process 3 (dimensionless)
DF4	=	dilution factor for process 4 (dimensionless)

Dilution Factor 1

Dilution factor 1 (DF1) is the ratio of the concentration of a contaminant in soil to the concentration in leachate that is in contact with the soil. This "dilution factor" represents the three phase partitioning between contaminant sorbed to soil, contaminant dissolved in pore water (*i.e.*, as leachate), and contaminant present as soil vapour. DF1 is calculated using the following equation:

$$DFI = K_{oc} \times f_{oc} + \frac{(\theta_w + H' \times \theta_a)}{\rho_b}$$

where:

DF1	=	dilution factor 1 (L/kg)
K _{oc}	=	organic carbon-water partition coefficient (L/kg)
foc	=	fraction organic carbon (g/g)
$\theta_{\rm w}$	=	water filled porosity (dimensionless)
H′	=	dimensionless Henry's Law constant (dimensionless)
θ_a	=	air filled porosity (dimensionless)
$ ho_b$	=	dry soil bulk density (g/cm ³)

Dilution Factor 2

Dilution factor 2 (DF2) is the ratio of the concentration of a contaminant in leachate that is in contact with the soil, to the concentration in pore water just above the groundwater table. DF2 takes the value 1.00 (*i.e.*, no dilution) for generic guidelines because it is assumed at Tier 1 that the contaminated soil extends down to the water table. Note that DF2 can be calculated on a site-specific basis at Tier 2 (AENV, 2009b).

Dilution Factor 3

Dilution factor 3 (DF3) is the ratio of the concentration of a chemical in pore water just above the groundwater table, to the concentration in groundwater beneath the source. This dilution factor reflects a decrease in concentration as leachate mixes with uncontaminated groundwater. DF3 is a function of groundwater velocity, infiltration rate, source length, and mixing zone thickness. The mixing zone thickness is calculated as being due to two processes: i) mixing due to dispersion, and ii) mixing due to infiltration rate. The equations used are as follows:

$$DF3 = 1 + \frac{Z_d \times V}{I \times X}$$
$$Z_d = r + s$$
$$r = 0.01 \times X$$
$$s = d_a \left\{ 1 - exp\left(\frac{-2.178 \times X \times I}{V \times d_a}\right) \right\}$$
$$V = K \times i$$

where:

DF3	=	dilution factor 3 (dimensionless)
Z_d	=	average thickness of mixing zone (m)
V	=	Darcy velocity in groundwater (m/year)
Ι	=	infiltration rate (m/year)
Х	=	length of contaminated soil (m)
r	=	mixing depth due to dispersion (m)
S	=	mixing depth due to infiltration rate (m)
da	=	unconfined aquifer thickness (m)
Κ	=	aquifer hydraulic conductivity (m/year)
i	=	lateral hydraulic gradient in aquifer (dimensionless)

Note that the parameter Z_d takes the fixed value of 2 m for the drinking water pathway, but is calculated for all other pathways.

Dilution Factor 4

Dilution factor 4 (DF4) accounts for the processes of dispersion and biodegradation as groundwater travels downgradient from beneath the source of contamination, and is the ratio of the concentration of a chemical in groundwater beneath the source, to the concentration in groundwater at a distance of 10 m (at Tier 1 for aquatic life) downgradient of the source. Consistent with AENV (2009a), the time independent version of the equation to calculate DF4 was used:

$$DF4 = \frac{2}{\exp(A) \times [erf(C) - erf(D)]}$$

$$A = \frac{x}{2D_x} \left\{ I - \left(I + \frac{4L_s D_x}{v}\right)^{1/2} \right\}$$
$$C = \frac{y + Y/2}{2(D_y x)^{1/2}}$$
$$D = \frac{y - Y/2}{2(D_y x)^{1/2}}$$
$$L_s = \frac{0.6931}{t_{1/2s}} \times \exp(-0.07d)$$
$$v = \frac{V}{\theta_t R_s}$$
$$R_s = I + \frac{\rho_b K_{oc} f_{oc}}{\theta_t}$$
$$D_x = 0.1x$$
$$D_y = 0.01x$$

where:

DF4	=	dilution factor 4 (dimensionless)	
erf	=	the error function	
А	=	dimensionless group A (dimensionless)	
С	=	dimensionless group C (dimensionless)	
D	=	dimensionless group D (dimensionless)	
Х	=	distance to source (10 m, aquatic life and wildlife watering, 0 m	
		other water uses)	
D _x	=	dispersivity in the direction of groundwater flow (m)	
Ls	=	decay constant (1/year)	
v	=	velocity of the contaminant (m/year)	
у	=	distance to receptor perpendicular to groundwater flow (m)	
Y	=	source width (m)	
Dy	=	dispersivity perpendicular to the direction of groundwater flow	
		(m)	
t _{1/2s}	=	decay half-life of contaminant in saturated zone of aquifer (years)	
d	=	water table depth (m)	

V	=	Darcy velocity in groundwater (m/year)
θ_t	=	total soil porosity (dimensionless)
R_{s}	=	retardation factor in saturated zone (dimensionless)
ρ_b	=	dry soil bulk density (g/cm ³)
K _{oc}	=	organic carbon partition coefficient (mL/g)
\mathbf{f}_{oc}	=	fraction organic carbon (g/g)

Aquatic Life

Substituting appropriate values from Tables 3, 5, 6, and 8 into this equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives values of:

- 65 mg/kg (DEG, coarse soil; Table 9);
- 2,000 mg/kg (DEG, fine soil; Table 10);
- 200 mg/kg (TEG, coarse soil; Table 11); and,
- 10,000 mg/kg (TEG, fine soil; Table 12).

Protection of Domestic Use Aquifer

Substituting appropriate values from Tables 3, 5, 6, and 8 into this equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives values of:

- 15 mg/kg (DEG, coarse soil; Table 9);
- 10 mg/kg (DEG, fine soil; Table 10);
- 150 mg/kg (TEG, coarse soil; Table 11); and,
- 100 mg/kg (TEG, fine soil; Table 12).

13.2 Groundwater Remediation Guidelines

Groundwater remediation guidelines for groundwater pathways were calculated using the model and equations from AENV (2009a).

13.2.1 Potable Groundwater

If contaminated groundwater is considered a domestic use aquifer, there is no offset assumed between contamination and a potential future water well, and therefore the Source Guidance Value for Groundwater (DEG = 6 mg/L; TEG = 60 mg/L) applies directly to groundwater (Tables 13 and 14).

13.2.2 Aquatic Life

Assumptions implicit in the model include the following:

- the soil/aquifer material in the saturated zone is physically and chemically homogeneous;
- decay of the contaminant source is not considered (*i.e.*, infinite source mass);
- the contaminant is not present as a free phase product;
- groundwater flow is uniform and steady;
- co-solubility and oxidation/reduction effects are not considered;
- dispersion is assumed to occur in the longitudinal and transverse directions only and diffusion is not considered; and,
- dilution of the plume by groundwater recharge down-gradient of the source is not considered.

Guideline Calculation

The groundwater remediation guideline protective of aquatic life is calculated using the following equations.

$$GWQG_{GR} = SWQG \times DF4$$

where:	$GWQG_{GR} =$	groundwater quality guideline protective of aquatic life (mg/L)
	$SWQG_{FL} =$	surface water quality guideline protective of aquatic life (mg/L)
	DF4 =	dilution factor for process 4 (L/kg)

Dilution factor 4 is calculated in the same way as described in Section 13.1.2

Substituting appropriate values from Tables 3, 5, 6, and 8 into this equation and rounding to 1 significant figure with a 5 or 0 in the second figure gives values of:

- 200 mg/L (DEG, coarse soil; Table 13);
- 4,000 mg/L (DEG, fine soil; Table 13);
- 550 mg/L (TEG, coarse soil; Table 14); and,
- 25,000 mg/L (TEG, fine soil; Table 14).

14. REFERENCES

(See also References in Appendices A, B, and C)

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