Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health

Methanol 2017

Methanol (CH_3OH; CAS 67-56-1) is a colourless, polar organic solvent with a molecular mass of 32.04 and a soil adsorption coefficient (K_{OC}) of 0.27. It is miscible with water.

Canada's methanol production capacity was 470,000 tonnes per year in 2012 (Cheminfo Services 2014). Actual production fluctuates with the cost of feedstocks and the product in world

Table 1a. Soil Quality Guidelines for Methanol: Coarse Soil, mg/kg dry weight

	Land use			
	Agricultural	**Residential/ parkland**	**Commercial**	**Industrial**
Guideline	**4.6**	**4.6**	**4.6**	**4.6**
Human health soil quality guideline	4.6*	4.6*	4.6*	4.6*
Limiting pathway	Groundwater check (drinking water)	Groundwater check (drinking water)	Groundwater check (drinking water)	Groundwater check (drinking water)
Environmental soil quality guideline	7.7*	7.7*	7.7*	7.7*
Limiting pathway	Groundwater check (aquatic life)	Groundwater check (aquatic life)	Groundwater check (aquatic life)	Groundwater check (aquatic life)

* Data are sufficient and adequate to calculate a soil quality guideline for human health and a soil quality guideline for protection of the environment. Therefore, the soil quality guideline is the lower of the two and represents a fully integrated new guideline for this land use, derived in accordance with the soil protocol (CCME 2006).

Table 1b. Soil Quality Guidelines for Methanol: Fine Soil, mg/kg dry weight

	Land use			
	Agricultural	**Residential/ parkland**	**Commercial**	**Industrial**
Guideline	**5.6**	**5.6**	**5.6**	**5.6**
Human health soil quality guideline	5.6*	5.6*	5.6*	5.6*
Limiting pathway	Groundwater check (drinking water)	Groundwater check (drinking water)	Groundwater check (drinking water)	Groundwater check (drinking water)
Environmental soil quality guideline	190*	190*	190*	190*
Limiting pathway	Groundwater check (aquatic life)	Groundwater check (aquatic life)	Groundwater check (aquatic life)	Groundwater check (aquatic life)

* Data are sufficient and adequate to calculate a soil quality guideline for human health and a soil quality guideline for protection of the environment. Therefore, the soil quality guideline is the lower of the two and represents a fully integrated new guideline for this land use, derived in accordance with the soil protocol (CCME 2006).

markets.

Human releases of methanol into the environment come primarily from solvent use, methanol production, end-product manufacturing, and bulk storage and handling losses. In 2013 15,385 tonnes of methanol were released to Canada's environment by major industrial sources, of which 13,000 tonnes were released to the air, 2,300 to water and 85 to land (Environment Canada 2013). The major emitters were pulp and paper, chemical manufacture, oil and gas, and waste treatment facilities.

Methanol occurs naturally in humans, animals and plants. It is a natural constituent of blood, urine, saliva and exhaled air, and it has been found in breast milk. Humans have a background body burden of 0.5 mg/kg body weight. Natural emission sources of methanol include volcanic gasses, vegetation, microbes and insects.

Sorption of methanol to soil particles is low, with methanol partitioning preferentially into porewater. The high water solubility of methanol, in combination with its very low soil adsorption coefficient, provides potential for high concentrations of methanol to be present in soil porewater, and for methanol in soil porewater to be highly mobile. A 1994 field study by the American Petroleum Institute (1994) found the half-life of methanol in groundwater to be approximately 245 days.

Behaviour and Effects in Biota

Although methanol occurs naturally in plants and animals, too much methanol can be poisonous. In cases of human methanol poisoning, the minimum lethal dose is in the range of 300 to 1,000 mg/kg of body weight (National Toxicology Program Center for the Evaluation of Risks to Human Reproduction 2004). Studies with non-human primates have typically yielded lethal doses in the range of 3,000 to 7,000 mg/kg of body weight. Table 2 summarises methanol toxicity effects in other biota.

Table 2. Effects of Methanol in Plants and Invertebrates*

Taxon	Lowest effect value (mg/kg in soil)	Effects (value given is the EC_{25})
Medicago sativa (alfalfa)	1,808	Depressed growth
Hordeum vulgare (barley)	2,538	Depressed growth
Elymus lanceolatus (northern wheatgrass)	2,877	Depressed growth
Eisenia andrei (earthworm)	9,756	Depressed growth
Folsomia candida (springtail)	2,842	Reduction in the number of viable offspring

* Stantec Consulting Ltd., 2006

Health Effects in Humans and Experimental Animals

In humans and primates, symptoms of methanol toxicity include blurred vision and blindness, convulsions, tremors, coma, nausea, headache, dizziness, abdominal pain, diminished motor skills, acidosis, dyspnea, behavioural and emotional deficits, and speech impediments. Methanol can be toxic to mouse and rat embryos around the seventh day of gestation. Effects include skeletal abnormalities, reduced organ weight and developmental defects. Health Canada has not reviewed the toxicity of methanol or developed a tolerable daily intake or tolerable concentration for methanol.

The United States Environmental Protection Agency (EPA) (2013) has developed an inhalation reference concentration (equivalent to a tolerable concentration) of 20 mg/m^3 for methanol. Its approach involved the calculation of four candidate inhalation reference concentration values from combinations of different studies, endpoints and benchmark response levels. The lowest value was selected as the inhalation reference concentration. The Canadian Council of Ministers of the Environment (CCME) has adopted this value as the tolerable concentration in the calculation of soil quality guidelines for methanol.

The EPA noted significant limitations in the oral database for methanol, and opted to derive an oral reference dose by using relevant inhalation data and route-to-route extrapolation with the aid of the EPA's physiologically based pharmacokinetic model. This approach was felt to be appropriate because methanol absorption has been shown to be rapid and essentially complete by both the oral and inhalation routes of exposure, and, once absorbed, it distributes rapidly to all organs and tissues according to water content, regardless of route of exposure. The EPA calculated an oral reference dose for methanol using the same four combinations of critical effects and response levels as used for the inhalation reference concentration. The lowest of the four candidate oral reference dose values (rounded to one significant figure) was 2 mg/kg per day. CCME has adopted this value as the tolerable daily intake in the calculation of soil quality guidelines for methanol.

Guideline Derivation

Canadian soil quality guidelines are derived for different land uses using different receptors and exposure scenarios for each land use (see Table 1). Table 3 (next page) provides the soil quality guidelines and check values for all uses. The scientific criteria document for methanol (CCME 2017) provides detailed derivations for methanol soil quality guidelines.

Soil Quality Guidelines for Environmental Health

CCME bases the environmental soil quality guidelines on soil contact data from toxicity studies on plants and invertebrates in soil, as well as considering the protection of aquatic life. In the case of agricultural land use, soil and food ingestion toxicity data for livestock are also included. To provide a broader scope of protection, CCME calculates a nutrient and energy cycling check, if sufficient data are available, and an off-site migration check for commercial and industrial land uses.

Table 3. Soil Quality Guidelines and Check Values for Methanol, mg/kg

	Land use			
	Agricultural	**Residential/ parkland**	**Commercial**	**Industrial**
Recommended guideline				
Coarse soil	4.6*	4.6*	4.6*	4.6*
Fine soil	5.6*	5.6*	5.6*	5.6*
Human health guidelines/check values				
SQG_{HH}				
Coarse soil	4.6	4.6	4.6	4.6
Fine soil	5.6	5.6	5.6	5.6
Direct contact	8,900	8,900	13,000	64,000
Protection of indoor air quality				
Coarse soil	3,800	3,800	40,000	40,000
Fine soil	100,000	100,000	490,000	490,000
Protection of potable water				
Coarse soil	4.6	4.6	4.6	4.6
Fine soil	5.6	5.6	5.6	5.6
Produce, meat and milk check	NC‡	NC[c]	—	—
Off-site migration check	—	—	—	NC†
Environmental health guidelines/check values				
SQG_{E}				
Coarse soil	7.7	7.7	7.7	7.7
Fine soil	190	190	190	190
Soil contact guidelines	1,200	1,200	1,600	1,600
Protection of freshwater life				
Coarse soil	7.7	7.7	7.7	7.7
Fine soil	190	190	190	190
Nutrient and energy-cycling check	NC‡	NC‡	NC‡	NC‡
Off-site migration check	—	—	—	NC†
Management limit	750	750	750	750
Interim soil quality criterion (CCME 2006)	No value	No value	No value	No value

Notes: NC = not calculated. The dash indicates a guideline/check value that is not part of the exposure scenario for this land use and therefore was not calculated.

* Data are sufficient and adequate to calculate an environmental and a health guideline. Therefore, the soil quality guideline is the lower of the two and represents a fully integrated new guideline for this land use, derived in accordance with the soil protocol (CCME 2006).

† Not determined, since methanol is a volatile organic chemical.

‡ Data are insufficient/inadequate to calculate this value.

CCME calculated the methanol soil contact guideline from a species sensitivity distribution of plant and invertebrate toxicity data evaluated at the 25th percentile effect level. CCME used the 25th percentile of this distribution as the soil contact guideline for agricultural and residential/parkland uses and the 50th percentile for commercial and industrial land uses. No surface water guideline protective of freshwater aquatic life currently exists for methanol, and accordingly, CCME developed a guideline based on available toxicity data (CCME 2017). Data were insufficient to calculate a water quality guideline for the protection of marine aquatic life.

Data were also insufficient to calculate the nutrient and energy-cycling check or the soil and food ingestion check. The off-site migration guideline was not calculated, due to the volatility of methanol. The soil guideline protective of aquatic life was the lowest of the ecological guidelines/check values for methanol, and CCME recommends this as the environmental soil quality guideline for all land uses.

Soil Quality Guidelines for Human Health

CCME bases human health soil quality guidelines on human soil contact, inhalation of indoor air, the protection of potable water, and check values for off-site migration and ingestion of produce, meat, and milk.

For methanol, CCME's (2006) protocol was used together with the human tolerable daily intake of 2 mg/kg of body weight to calculate the human soil contact guideline. The soil guideline protective of potable water was calculated using the CCME protocol and a source guidance value for groundwater of 19 mg/L. The source guidance value was calculated as described in the scientific criteria document (CCME 2017) using the human tolerable daily intake value noted above. The produce, meat and milk check was not calculated, because methanol is not expected to accumulate in produce, meat or milk. The off-site migration guideline was not calculated, due to the volatility of methanol. The scientific criteria document provides details of the guideline and check value calculations (CCME 2017). The soil guideline protective of potable water was the lowest of the guidelines that was calculated, and CCME recommends this value as the soil quality guideline for human health.

Management Limit

Management limits are soil guidelines values that take into consideration issues beyond direct human or ecological toxicity. This includes issues such as aesthetics (odour, soil appearance), flammability, and risk of infrastructure damage. No information was available on methanol concentrations in soil that would lead to offensive odours or to infrastructure damage. However, data were available on the flammability of field soil samples contaminated with methanol (CCME 2017). Samples at 7,460 mg/kg and lower did not support combustion. A safety factor of 10 was applied to this concentration to set the value for the flammability check for methanol in soil to 750 mg/kg.

Soil Quality Guidelines for Methanol

The soil quality guidelines are the lower of the soil quality guideline for human health and the soil quality guideline for protection of the environment.

For coarse and fine soil in all land uses, the human health guidelines are lower than the environmental guidelines. Therefore, the human health guidelines become the recommended soil quality guidelines. The soil quality guidelines in Table 1 represent a fully integrated new guideline for each land use.

Formaldehyde is a potential degradation product of methanol. Environment Canada and Health Canada (2001) reviewed formaldehyde as a priority substance under the *Canadian Environmental Protection Act* and found it not likely to cause adverse effects to terrestrial or aquatic organisms. It was, however, found to contribute to the formation of ground-level ozone and to be a human carcinogen. No attempt has been made to include possible formaldehyde toxicity in the guidelines for methanol. However, formaldehyde should always be analysed at any site with a significant methanol release and the results managed on a site-specific basis.

References

American Petroleum Institute. 1994. Transport and fate of dissolved methanol, methyl-tertiary-butyl ether, and monoaromatic hydrocarbons in a shallow sand aquifer. API Publication 4601. American Petroleum Institute, Washington, DC.

Canadian Council of Ministers of the Environment (CCME). 1991. Interim Canadian environmental quality criteria for contaminated sites. CCME, Winnipeg, MB.

Canadian Council of Ministers of the Environment (CCME). 2006. A protocol for the derivation of environmental and human health soil quality guidelines. CCME, Winnipeg, MB.

Canadian Council of Ministers of the Environment (CCME). 2017. Scientific criteria document for the development of the Canadian soil quality guidelines for methanol: Protection of Environmental and Human Health. CCME, Winnipeg, MB.

Cheminfo Services. 2014. Bio based chemical import replacement initiative. Chemical markets and biochemical options for Alberta. Cheminfo Services Inc., Markham, ON. Retrieved from http://www.albertacanada.com/business/industries/industry-reports.aspx

Environment Canada and Health Canada. 2001. Priority substances list assessment report—methanol. Environment Canada and Health Canada, Ottawa, ON.

Environment Canada. 2013. National pollutant release inventory. Environment Canada, Ottawa, ON. Retrieved from http://www.ec.gc.ca/inrp-npri/

National Toxicology Program Center for the Evaluation of Risks to Human Reproduction. 2004. NTP-CERHR expert panel report on the reproductive and developmental toxicity of methanol. *Reprod. Toxicol.* **18**: 303–390.

Stantec Consulting Ltd. 2006. Ecotoxicity assessment of amines, glycols, and methanol to soil organisms. Report prepared for Petroleum Technology Alliance Canada. Stantec, Guelph, ON.

United States Environmental Protection Agency. 2013. Toxicological review of methanol (non-cancer). In support of summary information on the integrated risk information system (IRIS). Environmental Protection Agency, Washington, DC.

Reference listing:

Canadian Council of Ministers of the Environment. 2017. Canadian soil quality guidelines for the protection of environmental and human health: Methanol. In: Canadian environmental quality guidelines, 1999. Canadian Council of Ministers of the Environment, Winnipeg, MB.

For further scientific information, contact:

Environment and Climate Change Canada
Place Vincent Massey
351 St-Joseph Blvd.
Gatineau, QC K1A 0H3
Phone: 819-953-1550
E-mail: ceqg-rcqe@ec.gc.ca

Aussi disponible en français.

Excerpt from Publication No. 1299; ISBN 1-896997-34-1