

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

MERCURY (INORGANIC) 1999

his fact sheet provides Canadian soil quality guidelines for mercury (Hg) for the protection of environmental and human health (Table 1). Supporting scientific documents are also available (Environment Canada 1996; Health Canada 1996).

Background Information

Mercury (CAS 7439-97-6) is a dense silver-white metal that is liquid at room temperature and is characterized by low electrical resistivity, high surface tension, and high thermal conductivity (Andren and Nriagu 1979; Environment Canada 1981).

The two properties that largely determine the environmental behaviour of mercury are the high vapour pressure of liquid mercury, yielding hazardous vapour concentrations, and the relative insolubility of ionic and

organic forms. Mercury can exist in three stable oxidation states: elemental mercury (Hg^0 , Hg(0)), mercurous ion (Hg_2^{2+} , Hg(I)), and mercuric ion (Hg^{2+} , Hg(I)).

Mercury (II) can be oxidized to both inorganic and organic salts, such as chlorides, sulphates, and organomercury compounds. A wide range of organomercury compounds are present in the environment and are characterized by the attachment of mercury to one or two carbon atoms to form compounds of the type R-Hg-X and R-Hg-R', where R and R' represent the organic moiety, and X represents a halogen. The organic moiety may take the form of alkyl, phenyl, or methoxyethyl radicals (WHO 1976). A subclass of short-chained alkylmercurials, which include monomethyl (CH₃Hg⁺) and dimethylmercury ((CH₃)₂Hg), are the predominant organic mercury compounds found in natural systems. Dimethylmercury is less stable and more volatile than monomethyl compounds (Environment Canada 1981). Other organic forms of

Table 1. Soil quality guidelines for mercury (mg·kg¹).

	Land use				
	Agricultural	Residential/ parkland	Commercial	Industrial	
Guideline	6.6 ^a	6.6 ^a	24 ^a	50 ^a	
SQG_{HH} Limiting pathway for SQG_{HH}	6.6 Soil ingestion	6.6 Soil ingestion	24 Soil ingestion	99 Off-site migration	
Provisional SQG_{HH} Limiting pathway for provisional SQG_{HH}	NC ^b ND	NC ^b ND	NC ^b ND	NC ^b ND	
SQG _E Limiting pathway for SQG _E	12 Soil contact	12 Soil contact	50 Soil contact	50 Soil contact	
Provisional SQG _E Limiting pathway for provisional SQG _E	NC ^c ND	NC ^c ND	NC ^c ND	NC ^c ND	
Interim soil quality criterion (CCME 1991)	0.8	2	10	10	

Notes: NC = not calculated; ND = not determined; $SQG_E = soil$ quality guideline for environmental health; $SQG_{HH} = soil$ quality guideline for human health.

The guidelines in this fact sheet are for general guidance only. Site-specific conditions should be considered in the application of these values. The values may be applied differently in various jurisdictions. The reader should consult the appropriate jurisdiction before application of the values.

^aData are sufficient and adequate to calculate an SQG_{HH} and an SQG_E. Therefore the soil quality guideline is the lower of the two and represents a fully integrated de novo guideline for this land use, derived in accordance with the soil protocol (CCME 1996a). The corresponding interim soil quality criterion (CCME 1991) is superseded by the soil quality guideline.

^bBecause data are sufficient and adequate to calculate an SQG_{HH} for this land use, a provisional SQG_{HH} is not calculated.

^CBecause data are sufficient and adequate to calculate an SQG_E for this land use, a provisional SQG_E is not calculated.

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mercury are phenylmercuric acetate (PMA), phenylmercuric chloride (PMC), methylmercuric dicyandiamide (MMD), methylmercuric acetate (MMA), and methylmercuric chloride (MMC).

The vapour pressure of mercury is highly dependent on temperature, and the tendency of liquid mercury to form small droplets increases its rate of evaporation. Mercury is found in the environment, not as the liquid metal, but mainly in the form of amalgams and inorganic salts, which have lower vapour pressures than elemental mercury (Andren and Nriagu 1979). The solubility of mercury compounds in water increases in the order: elemental mercury < mercurous chloride < methylmercury chloride < mercuric chloride. The toxicity of the inorganic forms is generally less than that of the organic compounds. Within the inorganic forms, toxicity increases as lipid solubility increases (Halbach 1990).

A number of mercury compounds were widely used in agriculture, medicine, and industry in Canada and have contributed to environmental contamination. However, there has been no Canadian production of mercury since 1975. Total Canadian anthropogenic emissions to the atmosphere were estimated at 39 855 kg, with the major source being base metal recovery (40%) (Environment Canada 1981). In 1989, Canada imported 32 442 kg of mercury and consumed 27 364 kg (Energy, Mines and Resources Canada 1990). Worldwide production figures for mercury indicate generally declining use (Fergusson 1990; ATSDR 1994).

The average terrestrial concentration of mercury in the Canadian environment is in the range of 0.01 to 0.4 mg·kg¹ (Jonasson and Boyle 1972; Gracey and Stewart 1974; McKeague and Kloosterman 1974; Environment Canada 1979; OMEE 1994), except in areas of ore deposits, spills, landfills, and accidents at metal-processing plants.

Frank et al. 1976 observed mercury concentrations ranging from 0.01 to 1.14 mg·kg⁻¹ in Ontario agricultural soils, with a mean of 0.11 mg Hg·kg⁻¹. In surface soil samples from areas not impacted by local point sources of pollution throughout Ontario, the 98th percentiles of mercury concentration measurements are 0.13 and 0.18 mg·kg⁻¹ for rural parkland and old urban parkland soils, respectively (OMEE 1993).

In Alberta soils, background mercury levels ranging from 0.01 to 0.135 mg·kg¹ have been reported (Dudas and Pawluk 1976; Dudas and Cannon 1983; George et al. 1994). Elevated mercury levels are common in British Columbia due to the cinnabar deposits. High soil mercury levels are also reported in Quebec and Ontario near areas of known gold, copper, or zinc mineralization (Environment Canada 1979).

Environmental Fate and Behaviour in Soil

The major soil factors that determine the fate and behaviour of mercury are pH, organic matter and clay content, redox potential, cation exchange capacity (CEC), aeration, and texture. The major processes that determine the mobility and distribution of mercury in the terrestrial environment are adsorption, chemical reactions, leaching, volatilization, photolysis, and biodegradation. These processes are dependant on the soil factors mentioned above

In soils, mercury occurs mainly in the Hg⁰ and Hg²⁺ valence states. Depending on redox conditions, the dimeric ion (Hg₂²⁺) may also be encountered. The speciation of mercury in soils also depends on the pH and the concentration of chloride ions. Under natural conditions, most of the Hg²⁺ in the soil is either bound in the soil minerals or adsorbed onto organic or inorganic solids, with only a very small portion present in the soil solution (Steinnes 1995).

Adsorption is the dominant process determining mercury's fate in the terrestrial environment (Hogg et al. 1978). It depends on mercury's chemical form, soil pH, colloids, CEC, and redox potential (Hogg et al. 1978; Kabata-Pendias and Pendias 1992). Adsorption is increased by the presence of organic matter due to mercury complexation with humic and fulvic acids, and therefore it is greater in surface horizons due to high humus content (Lodenius et al. 1987). Adsorption is maximized at pH 4-5 (Thanabalasingam and Pickering 1985; Semu et al. 1986) and is decreased by Cl⁻ ions (Andersson 1979). In neutral and low organic matter soils, it depends on iron and clay minerals as important adsorption sites (OECD 1993). When added in elemental, cationic, or anionic forms, mercury strongly adsorbs to soils (Kabata-Pendias and Pendias 1992).

Mercury undergoes methylation by aerobic and anaerobic bacteria (NRCC 1979; WHO 1991). Methyl mercury species are mobile, bioavailable, and highly toxic (Lexmond et al. 1976; Bigham and Henry 1993). Under reduced conditions, mercury and sulphide ions form HgS, an insoluble salt that is resistant to methylation. Under aerobic conditions, HgS is oxidized to the sulphate form HgSO₄, which can undergo methylation. Bacterial action can cause demethylation of methyl mercury compounds. The chloride concentration and pH determine the chemical form of monomethylmercuric ion complexes (NRCC 1979).

Leaching of mercury occurs in soils with little or no organic matter and light texture. Chloride complexes of mercury are soluble and, hence, subject to leaching. In acid soils, mercury is leached out in a bound form with

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organic matter, whereas in neutral and alkaline soils, mercury is leached out in an inorganic active form (Kabata-Pendias and Pendias 1992). Acid rain increases leaching of mercury (Lodenius et al. 1987). Highest leaching of mercury occurs in spring and autumn (Jonasson and Boyle 1972).

Volatilization is due to chemical and biological transformations of mercury compounds in soils (Frear and Dills 1967; Rogers and McFarlane 1979). The main form of mercury in the air is elemental mercury, but dimethylmercury may also occur (Lindberg et al. 1987; WHO 1989). Volatilization increases with pH and temperature, but also depends on organic matter content, redox potential, moisture content, and pore space of the soil (Frear and Dills 1967). Under favourable conditions, 50% of added mercury has volatilized within a week (Gilmour and Miller 1973).

Monomethylmercury may decompose photolytically to elemental mercury and methyl radicals (NRCC 1979). Dimethylmercury may be transformed to the mono form at low pH by ultraviolet light (Jernelov 1975). Photolysis of mercury chloride compounds may result in the production of methylmercury ions, dimethylmercury, and metallic mercury (Jewett et al. 1975).

Mercury is subject to biotic and abiotic transformations in soils (Andersson 1979; Kabata-Pendias and Pendias 1992). Both aerobic and anaerobic soil microbes can convert elemental mercury to mono and then to dimethylmercury. On the other hand, soil microbes are also capable of converting organic mercury to elemental mercury, but this is a slower process (Kabata-Pendias and Pendias 1992). *Clostridium* species, under anaerobic conditions, transform several mercury species (except HgS) to methylmercury (Yamada and Tonomura 1972). *Pseudomonas* species are mainly responsible for degrading organic and inorganic mercurials to metallic mercury (Furukawa and Tonomura 1972). Methylmercury is stable in soils (Rundgren et al. 1992).

Behaviour and Effects in Biota

Soil Microbial Processes

Von Stadelmann and Santschi-Fuhrimann (1987) reported that the lowest content of total mercury at which effects were detected (25% reduction in microbial respiration) is in the range of 0.06 to 0.08 mg Hg·kg⁴ soil. Wilke (1988) observed similar effects at 1.3 mg Hg·kg⁴ in soils. The soluble fractions in both studies were the same, 0.02 mg Hg·kg⁴ (Lindqvist 1991).

Mercury concentrations that have been shown to reduce microbial CO₂ production in soil range from 0.1 mg·kg¹ for a 16% reduction to 400 mg·kg¹ for a 69% reduction (Van Faassen 1973; Cornfield 1977; Landa and Fang 1978; Zelles et al. 1985, 1986; Tu 1988).

Reductions in soil nitrogen mineralization have been reported at concentrations ranging from 6 to 1003 mg Hg·kg¹ (Van Faassen 1973; Liang and Tabatabai 1977; Wilke 1989).

Studies have also shown that nitrification has been reduced by 8% at 50 mg Hg·kg¹ soil, by 21% at 200 mg Hg·kg¹ soil, and by 94–98% at 1003 mg Hg·kg¹ soil (Liang and Tabatabai 1978; Wilke 1989).

Terrestrial Plants

Common symptoms of mercury toxicity to plants are inhibition of photosynthesis, stunted roots, and stunted seedlings, all with consequent reductions in yield. Some studies reported that the accumulation of mercury in roots inhibits uptake of other elements, such as potassium (Kabata-Pendias and Pendias 1992).

The lowest soil concentrations at which phytotoxic effects have been observed are 7 and 8 mg Hg·kg¹, which resulted in a 50% reduction in the first bloom of turnips and decreased growth (not quantifiable) of Bermuda grass (Weaver et al. 1984; Sheppard et al. 1993).

The literature shows that a variety of growth endpoints are reduced by 50% at concentrations ranging from 7 to 1000 mg Hg·kg⁴ soil (Sheppard et al. 1993; Environment Canada 1995). Twenty-five percent reductions in seedling emergence of lettuce and radishes occurred at 11 and 73 mg Hg·kg⁴ soil, respectively (Environment Canada 1995).

Macnicol and Beckett (1985) established the critical level of mercury tissue content leading to depression of yield, between 1 and 8 mg·kg¹ dw of tissue for barley, cabbage, maize, and oats.

Terrestrial Invertebrates

Mercury accumulates in soil invertebrates even at low soil concentrations (Rundgren et al. 1992). Mercury concentrations in invertebrates ranging from 0.79 mg·kg¹ for harvestman (*Phalangida*) to 15.5 mg·kg¹ for earthworms (*Oligochaeta*) have been reported by Talmage and Walton (1993) in a mercury-contaminated site. Mean

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food chain transfer coefficients, defined as the ratio of mercury concentration in the whole body to mercury concentration in food, were 0.88 for herbivore/omnivore invertebrates and 2.35 for carnivore invertebrates.

Earthworms have suffered 25% mortality in soil at mercury concentrations ranging from 130 to 250 mg·kg⁴, while concentrations resulting in 50% mortality range from 60 to 700 mg·kg⁴ in varying soil types (Fisher and Koszorus 1992; Sheppard et al. 1993; Environment Canada 1995).

Livestock and Wildlife

In mammals and birds, mercury is usually absorbed through the gastrointestinal tract and through the lungs (WHO 1976; NRCC 1979). Mercury levels are generally highest in the kidney and liver tissues (NRCC 1979; WHO 1989). Brain tissue also absorbs mercury in vapour and organic forms (Aschner and Aschner, 1990). The principal routes of elimination of mercury from the body are through the urine and feces.

Hill and Soares (1984) provide the only toxicological study using inorganic mercury. The LC₅₀ for *Coturnix* (*Cotornix japonica*) was 1751 mg·kg⁴ bw per day. All of the other livestock and wildlife studies found reported the toxicological effects of organic mercury compounds.

Human and Experimental Animal Health Effects

The pharmacokinetics and toxicological effects of inorganic mercury compounds have been comprehensively reviewed by WHO (1991), ATSDR (1994), and Health and Welfare Canada (1986) and will not be reiterated here.

The International Agency for Research on Cancer working group on the evaluation of carcinogenic risk to humans classified inorganic mercury compounds as "not classifiable as to their carcinogenicity to humans" (Group 3) on the basis of inadequate evidence in humans for the carcinogenicity of mercury and mercury compounds and limited evidence in experimental animals for the carcinogenicity of mercuric chloride (IARC 1993). Although using the same weight of evidence as WHO (1993), the U.S. Environment Protection Agency (IRIS 1996) recently classified mercuric chloride as a possible human carcinogen (Group C). Inorganic mercury compounds have not been classified by Health Canada with respect to human carcinogenicity.

The kidney is the critical organ following the ingestion of inorganic divalent mercury salts (WHO 1991; NTP 1993). The most sensitive adverse effect on the kidney in animal studies is the formation of mercury-induced auto-immune glomerulonephritis, the first step of which is the production and deposition of IgG (immunoglobulin G) antibodies on the glomerular basement membrane (WHO 1991; IRIS 1996). This effect has been consistently observed in studies using the brown Norway rat, a strain considered to be the most sensitive for this endpoint (WHO 1991: IRIS 1996). Laboratory studies using mice (Hultman and Enestrom 1992) and rabbits (Lindqvist et al. 1974), as well as clinical studies (WHO 1991), have also demonstrated the same critical effect after exposure to relatively low doses of inorganic divalent mercury salts by various routes.

In 1995, after an extensive review and workshop discussions of the entire database of studies on inorganic mercury compounds, the U.S. Environment Protection Agency affirmed the oral reference dose (RfD) for inorganic mercury (mercuric chloride) established in 1985 (IRIS 1996). This oral RfD of 0.0003 mg·kg⁻¹ bw per day is based on the back calculations from a drinking water equivalent level (DWEL) of 0.10 mg·L⁴, assuming a water consumption rate of 2 L per day and a body weight of 70 kg. The DWEL was recommended on the basis of the weight of evidence from three key studies using the brown Norway rat (Druet et al. 1978; Bernaudin et al. 1981; Andres 1984) and limited human tissue studies. In those studies, brown Norway rats were administered mercuric chloride by subcutaneous injection (Druet et al. 1978) or by gavage in water (Bernaudin et al. 1981: Andres 1984). The LOAEL doses were determined to be 0.226 mg·kg⁻¹ bw per day (after conversion from subcutaneous route (100% absorption) to oral route (7%) (Health Canada 1996), 0.317 mg·kg⁴ bw per day (Bernaudin et al. 1981), and 0.633 mg·kg⁴ bw per day (Andres 1984). An uncertainty factor of 1000 was applied (10 for the use of subchronic studies, a combined 10 for both animal to human and sensitive human populations and 10 for the use of LOAELs instead of NOAELs); no modifying factor was used.

Other agencies such as the World Health Organization (WHO 1993) and (Health and Welfare Canada 1986) have conservatively based their drinking water guidelines for mercury (as total) on the neurological effects of methyl mercury in human populations; hence, no TDIs were derived for inorganic mercury. The oral RfD of 0.0003 mg·kg¹ bw per day as inorganic divalent mercury, recently reaffirmed by the U.S. Environment Protection Agency (IRIS 1996), is therefore adopted as an oral TDI for the derivation of human health soil quality guidelines.

Guideline Derivation

Canadian soil quality guidelines are derived for different land uses following the process outlined in CCME (1996a) using different receptors and exposure scenarios for each land use (Table 1). Detailed derivations of the soil quality guidelines for mercury are provided in Environment Canada (1996) and Health Canada (1996).

Soil Quality Guidelines for Environmental Health

Environmental soil quality guidelines (SQG_{ES}) are based on soil contact using data from toxicity studies on plants and invertebrates. In the case of agricultural land use, soil and food ingestion toxicity data for mammalian and avian species are included. To provide a broader scope of protection, a nutrient and energy cycling check is calculated. For industrial land use, an off-site migration check is also calculated.

For all land uses, the preliminary soil contact value (also called threshold effects concentration [TEC] or effects concentration low [ECL], depending on the land use) is compared to the nutrient and energy cycling check. If the nutrient and energy cycling check is lower, the geometric mean of the preliminary soil contact value and the nutrient and energy cycling check is calculated as the soil quality guideline for soil contact. If the nutrient and energy cycling check is greater than the preliminary soil contact value, the preliminary soil contact value becomes the soil quality guideline for soil contact.

For agricultural land use, the lower of the soil quality guideline for soil contact and the soil and food ingestion guideline is recommended as the SQG_E .

For residential/parkland and commercial land uses, the soil quality guideline for soil contact is recommended as the $SQG_{\rm E}$.

For industrial land use, the lower of the soil quality guideline for soil contact and the off-site migration check is recommended as the SQG_E.

In the case of mercury, the recommended SQG_E is based on the soil contact guideline for all land use categories (Table 2).

Soil Quality Guidelines for Human Health

Human health soil quality guidelines for threshold contaminants are derived using a TDI for the most sensitive receptor designated for a land use. The CCME recommends the application of various check mechanisms, when relevant, in order to provide a broader scope of protection. The lowest of the soil ingestion guidelines and any of the calculated checks is recommended as the $SQG_{\rm HH}$.

Soil Quality Guidelines for Mercury

For each land use category, the soil quality guideline for mercury is the lower of the SQG_{HH} and SQG_E (Table 1).

CCME (1996b) provides guidance on potential modifications to the final recommended soil quality guideline when setting site-specific objectives.

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Table 2. Soil quality guidelines and check values for mercury (mg·kg⁻¹).

	Land use				
	Agricultural	Residential/ parkland	Commercial	Industrial	
Guideline	6.6 ^a	6.6 ^a	24 ^a	50 ^a	
Human health guidelines/check values					
SQG_{HH}	6.6 ^b	6.6 ^b	24 ^b	99 ^b	
Soil ingestion guideline	6.6	6.6	24	690	
Inhalation of indoor air check	NC ^c	NC ^c	NC ^c	NC^c	
Off-site migration check	_	_	_	99	
Goundwater check (drinking water)	NC^d	NC^d	NC^d	NC^d	
Produce, meat, and milk check	NCe	NC ^e	_	_	
Provisional SQG _{HH} Limiting pathway for provisional SQG _{HH}	NC ^f ND	NC ^f ND	NC ^f ND	NC ^f ND	
Environmental health guidelines/check values					
SQG_E	12 ^g	12 ^g	50 ^g	50 ^g	
Soil contact guideline	12	12	50	50	
Soil and food ingestion guideline	NC^h	_	_	_	
Nutrient and energy cycling check	20	20	52	52	
Off-site migration check	_	_	_	142	
Groundwater check (aquatic life)	NC^d	NC^d	NC^d	NC^d	
Provisional SQG_E Limiting pathway for provisional SQG_E	NC ⁱ ND	NC ⁱ ND	NC ⁱ ND	NC ⁱ ND	
Interim soil quality criterion (CCME 1991)	0.8	2	10	10	

Notes: NC = not calculated; ND = not determined; $SQG_E = soil$ quality guideline for environmental health; $SQG_{HH} = soil$ quality guideline for human health. The dash indicates a guideline/check value that is not part of the exposure scenario for this land use and therefore is not calculated.

^aData are sufficient and adequate to calculate an SQG_{HH} and an SQG_E. Therefore the soil quality guideline is the lower of the two and represents a fully integrated de novo guideline for this land use, derived in accordance with the soil protocol (CCME 1996a). The corresponding interim soil quality criterion (CCME 1991) is superseded by the soil quality guideline.

^bThe SQG_{HH} is the lowest of the human health guidelines and check values.

^CApplies only to volatile organic compounds and is not calculated for metal contaminants.

dApplies to organic compounds and is not calculated for metal contaminants. Concerns about metal contaminants should be addressed on a site-specific basis.

^eApplies to nonpolar organic compounds and is not calculated for metal contaminants. Concerns about metal contaminants should be addressed on a site-specific basis.

fBecause data are sufficient and adequate to calculate an SQGHH for this land use, a provisional SQGHH is not calculated.

gThe SQG_E is the lowest of the environmental health guidelines and check values.

 $^{^{} ext{h}}$ There are insufficient data to calculate a soil and food ingestion guideline for inorganic mercury. Using data available for organic mercury, a soil and food ingestion guideline of 19 mg·kg⁻¹ soil has been calculated.

¹Because data are sufficient and adequate to calculate an SQG_E for this land use, a provisional SQG_E is not calculated.

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