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

COPPER
1999

This fact sheet provides Canadian soil quality guidelines for (total) copper (Cu) for the protection of environmental and human health (Table 1). A supporting scientific document is also available (CCME 1997).

Background Information

Copper (CAS 7440-50-8) is a metal that occurs in four oxidation states (Cu, Cu^{1+}, Cu^{2+}, and Cu^{3+}) with Cu^{2+} being most common. The atomic number and atomic weight of copper are 29 and 63.546, respectively. Copper has a specific gravity of 8.96 at 20°C, a melting point of 1083°C, and a boiling point of 2695°C (CCME 1997).

Copper is widely used in the manufacture of textiles, antifouling paints, electrical conductors, plumbing fixtures and pipes, coins, and cooking utensils. Copper compounds are found in wood preservatives, pesticides, and fungicides as an active ingredient, and copper sulphate may be used as a micronutrient in agricultural fertilizers (CCME 1997).

Copper occurs in a wide range of mineral deposit types and as both primary and secondary minerals. Elemental copper metal does occur in nature, but most copper occurs in the form of sulphide minerals, particularly chalcopyrite ($CuFeS_2$), as well as chalcocite (Cu_2S), bornite ($Cu_5 FeS_4$), and tetrahedrite ($(CuFe)_{12}Sb_4S_{13}$). As a result of chemical weathering of these primary copper sulphide minerals,

Table 1. Soil quality guidelines for total copper ($mg \cdot kg^{-1}$).

	Land use			
	Agricultural	**Residential/ parkland**	**Commercial**	**Industrial**
Guideline	**63**[a]	**63**[a]	**91**[a]	**91**[a]
SQG_{HH}	1100	1100	4000	16 000
Limiting pathway for SQG_{HH}	Soil ingestion	Soil ingestion	Soil ingestion	Off-site migration
Provisional SQG_{HH}	NC[b]	NC[b]	NC[b]	NC[b]
Limiting pathway for provisional SQG_{HH}	ND	ND	ND	ND
SQG_E	63	63	91	91
Limiting pathway for SQG_E	Soil contact	Soil contact	Soil contact	Soil contact
Provisional SQG_E	NC[c]	NC[c]	NC[c]	NC[c]
Limiting pathway for provisional SQG_E	ND	ND	ND	ND
Interim soil quality criterion (CCME 1991)	150	100	500	500

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

[a]Data are sufficient and adequate to calculate an SQG_{HH} and an SQG_E. Therefore the soil quality guideline is the lower of 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.

[b]Because data are sufficient and adequate to calculate an SQG_{HH} for this land use, a provisional SQG_{HH} is not calculated.

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

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.

secondary minerals may be formed, including the oxide mineral cuprite (Cu_2O), the carbonate minerals malachite ($Cu_2(CO_3)(OH)_2$) and azurite ($Cu_3(CO_3)_2(OH)_2$), and the sulphate minerals brochantite ($Cu_4SO_4(OH)_6$) and antlerite ($Cu_3SO_4(OH)_4$) (CCME 1997).

Copper concentrations in soil vary considerably with soil type, soil amendments, distance from anthropogenic sources, distance from natural ore bodies, and composition of bedrock and parent material among other factors. In general, however, the average copper concentration in Canadian soil is estimated to be 20 $mg \cdot kg^{-1}$, with a range between 2 and 100 $mg \cdot kg^{-1}$ (British Columbia Ministry of Environment, Lands and Parks 1992). McKeague and Wolynetz (1980) reported that, in general, soils from the Cordilleran Region contained the highest levels of copper (46 $mg \cdot kg^{-1}$), while those of the Canadian Shield contained the lowest (11 $mg \cdot kg^{-1}$). The mean copper level in the 173 samples analyzed from all regions was 22 $mg \cdot kg^{-1}$ (McKeague and Wolynetz 1980). The 98th percentile of copper concentrations in rural parkland and old urban parkland soils of Ontario not impacted by local point sources of pollution were 41 and 65 $mg \cdot kg^{-1}$, respectively (OMEE 1993). Soils sampled in the A and C horizons in southern and western Manitoba had an average copper concentration of 25 $mg \cdot kg^{-1}$ (Mills and Zwarich 1975). In rural Alberta soils, prior to application of municipal sewage sludge, the average copper concentration ranged from 17 to 19 $mg \cdot kg^{-1}$ (G. Lutwick 1995, Alberta Environmental Protection, Soil Protection Branch, pers. com.).

Surface soils in the immediate vicinity of copper smelters were found to be heavily contaminated by atmospheric fallout. Average total copper concentrations were often well above 1000 $mg \cdot kg^{-1}$ (Hutchinson and Whitby 1974; Hazlett et al. 1983; Kuo et al. 1983).

Mean copper concentrations in roadside soils from Moncton, New Brunswick, were 45 $mg \cdot kg^{-1}$ and ranged from 6 to 162 $mg \cdot kg^{-1}$ (Cool et al. 1980). In general, street and highway dusts contained higher copper concentrations than the corresponding roadside soils. Moreover, higher copper levels were usually found in dusts from more urbanized and industrialized centres. For example, street dusts from Halifax, Nova Scotia, contained an average of 86.5 $mg \cdot kg^{-1}$ of copper, ranging from 54 to 119 $mg \cdot kg^{-1}$ (Ferguson and Ryan 1984), while copper levels in street dusts from metropolitan Cincinnati, Ohio, were much higher (range of means 910–1883 $mg \cdot kg^{-1}$) (Tong 1990).

The analytical method recommended for total copper by the CCME is the U.S. Environmental Protection Agency Method 6010, Revision 0, Inductively Coupled Plasma-Atomic Emission Spectroscopy, for the determination of trace elements in groundwater, soils, sludges, sediments, and other waste solids (CCME 1993). The detection limit for this method is 0.6 $mg \cdot kg^{-1}$ of soil.

Environmental Fate and Behaviour in Soil

Copper is strongly adsorbed to soil particles and therefore has very little mobility relative to other trace metals (Alloway 1990). As a result of this limited mobility, applied copper tends to accumulate in soil (Slooff et al. 1989). Soil types have finite holding capacities for copper ions, and leaching can occur when the copper levels applied exceed this capacity (Adriano 1986).

Soil factors that influence the availability of copper in soils are pH, cation exchange capacity (CEC), organic matter content, presence of oxides of iron, manganese, and aluminum, and reduction–oxidation (redox) potential (Adriano 1986; Slooff et al 1989).

Adriano (1986) showed that the capacity of soil to adsorb copper increased with increasing pH, with a maximum holding capacity at neutral to slightly alkaline conditions (pH 6.7–7.8). Furthermore, soils with alkaline conditions tend to favour precipitation of copper; thus, copper is more mobile under acidic than alkaline conditions.

In general, the higher the CEC, the greater the amount of copper it can adsorb (Adriano 1986). Soils with a high CEC have the ability to remove trace metal cations from the soil solution (Fuller 1977). The CEC is influenced by the type and amount of clay present, the amount of organic matter present, and the pH of the soil (CCME 1997).

Copper has a very high affinity for organic matter and is more strongly bound than other trace elements (Nriagu 1979; Adriano 1986; Sloof et al. 1989; Alloway 1990). This high adsorption ability of organic matter is likely due to its high CEC and chelating ability (Adriano 1986; Hunter et al. 1987). Copper found in soil solution is often bound to dissolved organic matter and will only be released in an ionic form under strongly oxidizing conditions or through microbial degradation of the organic matter (Fuller 1977; Gibson and Farmer 1984). Even though organic matter generally contributes to copper's immobility through binding, it can also increase copper's solubility by forming soluble complexes (CCME 1997).

Copper is specifically adsorbed by iron, aluminum, and manganese oxides (Alloway and Jackson 1991). With the possible exception of lead, copper is the most strongly adsorbed of all the divalent transition and trace metals on iron and aluminum oxides and oxyhydroxides (Adriano 1986).

The water content of soils influences copper holding capacity through biotic and abiotic oxidation–reduction reactions. Reduction of copper results in increased solubility (Adriano 1986). According to Reddy and Patrick (1983), reduction can act to solubilize copper specifically adsorbed onto iron and manganese oxides and hydrous oxides.

Behaviour and Effects in Biota

Copper is an essential element required for good health and proper functioning of biological processes in plants and animals. Copper overexposure and deficiency can both have serious adverse effects. The recommended minimum dietary copper concentrations for calves, mink, and chickens are 10 $mg\cdot kg^{-1}$ dw, 4.5–6.0 $mg\cdot kg^{-1}$ dw, and 8–10 $mg\cdot kg^{-1}$ dw, respectively (Puls 1988). Toxic copper concentrations range from 40 to 100 $mg\cdot kg^{-1}$ bw, >200 $mg\cdot kg^{-1}$ bw, and 250–500 $mg\cdot kg^{-1}$ bw for calves, mink, and chickens, respectively (Puls 1988).

Soil Microbial Processes

The lowest copper concentration causing an adverse effect to carbon dioxide evolution in a microbial population was reported by Cornfield (1977). At a concentration of 100 mg $Cu\cdot kg^{-1}$, a 25% decrease in CO_2 evolution was observed.

Terrestrial Plants

The lowest soil copper concentration at which phytotoxic effects have been observed is 50 mg $Cu\cdot kg^{-1}$ in dry soil and resulted in an 18% decrease in radicle elongation in paper birch *(Betula papyrifera)*. No observed effect was noted in white pine *(Pinus strobus)*, white spruce *(Picea glauca)*, and red pine *(Pinus resinosa)* when exposed to 50 mg $Cu\cdot kg^{-1}$ dry soil (Patterson and Olson 1982). Typical symptoms of copper toxicity in plants include dark green leaves followed by induced iron chlorosis, thick, short or barbed-wire roots, and depressed tillering (Kabata-Pendias and Pendias 1991). Copper bioaccumulates to a small degree. A soil-to-plant BCF of 0.2645 was calculated from data on a variety of species (CCME 1997).

Terrestrial Invertebrates

The lowest copper concentrations at which adverse effects occur in soil invertebrates come from an investigation by Ma (1988) on cocoon production by three different types of earthworms *(Aporrectodea caliginosa*, *Allolobophora chlorotica*, and *Lumbricus rubellus)*. In *A. caliginosa* and *A. chlorotica*, cocoon production started to decline at a soil level of 28 mg $Cu\cdot kg^{-1}$, while in *L. rubellus* 80 mg $Cu\cdot kg^{-1}$ in soil was required to see a response. EC_{50} values of 51 $mg\cdot kg^{-1}$, 68 $mg\cdot kg^{-1}$, and 122 $mg\cdot kg^{-1}$ were reported for *A. chlorotica*, *A. caliginosa*, and *L. rubellus*, respectively. A soil-to-invertebrate BCF of 0.47 was also determined using data from literature studies (CCME 1997).

Livestock and wildlife

Livestock and wildlife have also been shown to react adversely to both high and deficient copper concentrations. Sheep are particularly sensitive to the complex interactions that exist between copper, sulphur, molybdenum, and to a lesser extent zinc and iron (CCME 1997). The National Research Council (NRC) outlined numerous difficulties in establishing minimum copper requirements for sheep due to genetic differences between breeds, individual differences within a breed, types of forage material, and the nutrient composition of the diet (NRC 1985). The band that separates hypocupremia from copper toxicity in sheep is very narrow. Levels of copper that may produce deficiencies in sheep under specific environmental conditions may be toxic to sheep given a different set of environmental conditions, such as decreased molybdenum and sulphur content of the diet. Researchers have observed acute toxicosis at dietary copper concentrations of 16–20 $mg\cdot kg^{-1}$ in lambs fed on low molybdenum diets (Adamson et al. 1969; White et al. 1989). Symptoms of copper toxicity in livestock and wildlife can include, but are not limited to, depression, anorexia, frequent recumbency, abdominal discomfort, jaundice, hemolytic crisis, hemoglobinuria, and hemoglobinemia.

Human and Experimental Animal Health Effects

The current database on copper concentrations in the Canadian environment is very extensive. Consequently, exposure estimates for the Canadian general population are well characterized. Estimates of total daily copper intake for Canadians (as total copper) range from about 22 to 74 μg·kg^{-1} bw per day in adults and formula-fed infants, respectively. Children aged 6 months to 4 years are estimated to ingest an average of 66 μg·kg^{-1} bw per day. For all age classes, diet is the major source of the element, with less significant amounts from drinking water. Soil, dust, and air were insignificant sources of exposure (CCME 1997).

The essentiality of copper has been demonstrated in a number of human and relevant experimental animal studies. Copper is required for many enzymatic reactions. Although insufficient data exist to allow the establishment of recommended daily dietary intakes, Health and Welfare Canada (1990) has listed dietary copper intakes that "seem to be adequate and safe" of 30 μg·kg^{-1} bw per day (2.0 mg·d^{-1}) in adults and ranging from 50 to 100 μg·kg^{-1} bw per day in 3- to 11-year-old children. Copper deficiency is quite rare in humans. Adverse health effects, some of which are serious (hypochromic anemia and central nervous system and cardiovascular system disturbances) have been observed in severely copper-deficient children and in experimentally induced copper-deficient adult volunteers (CCME 1997).

The regulation of copper balance in the body appears to be controlled by both absorption and excretion mechanisms. Copper absorption is strongly dependent on the levels of copper in the diet. When dietary levels of copper are low, the absorption of this element is increased. Conversely, with high dietary levels, absorption is reduced and an increase in endogenous excretion of copper is observed to maintain homeostasis. The ratio of copper to other dietary components (e.g., zinc, iron, and molybdenum) may be as important as the actual copper levels in the diet. In humans, an overall absorption rate of 25–40% at a dietary intake of 1–3 mg Cu·d^{-1} has been estimated. Factors that affect copper absorption include competition with other metals (zinc and cadmium), the amount of copper in the stomach, certain dietary components (e.g., ascorbic acid, phytate, and fibre), and the form of copper. The copper and molybdenum intake ratios appear to be very important and are probably related to intestinal absorption (CCME 1997).

Reports of acute copper poisoning in humans are scarce because of the strong emetic properties of this element; doses as low as 0.12 mg·kg^{-1} bw per day may induce nausea and vomiting in some individuals. The ingestion of gram quantities of inorganic copper salts is usually fatal in humans, but there is considerable variability in individual sensitivities (lethal dose range: 50–500 mg Cu·kg^{-1} bw per day) (CCME 1997).

The health effects associated with chronic exposure to elevated dietary copper levels in humans are not well documented. Chronic oral exposure resulting in adverse health effects is rare. A review of literature has identified three subgroups of the population that may be at a greater risk of chronic copper overexposure/loading: Wilson's disease patients (hereditary disease), individuals with glucose-6-phosphate dehydrogenase deficiencies, and young children, particularly those under 12 months of age, possibly because of their limited ability to excrete metals (CCME 1997).

Limited data in humans and experimental animals indicate that copper does not appear to be teratogenic or carcinogenic. Microbial mutation assays with various copper compounds are reported to be negative. Conflicting results from in vivo studies and mammalian system in vitro studies, however, suggest that copper may be potentially mutagenic (CCME 1997).

No conventional TDI was derived for copper since the use of an overall NOAEL is inappropriate in this case. Too many factors may affect the toxic potential of copper (e.g., chemical form, potential interaction with other micro elements and other components of the diet, health and nutritional status of individuals, etc.). The dietary copper requirements that "seem to be adequate and safe" (Health and Welfare Canada 1990) are therefore adopted as provisional TDIs for the derivation of human health soil quality guidelines (CCME 1997).

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. Detailed derivations for copper soil quality guidelines are provided in CCME (1997).

Soil Quality Guidelines for Environmental Health

The 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 also included. For the soil contact pathway, sufficient data are available to allow use of the preferred weight-of-evidence procedure. 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_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 copper, the recommended SQG_E is based on the soil contact guideline for all land uses (Table 2).

Soil Quality Guidelines for Human Health

Human health soil ingestion guidelines for threshold contaminants are derived using TDI for the most sensitive receptor designated for a land use. For copper, a provisional TDI is used in place of a conventional TDI.

The CCME recommends the application of various check mechanisms, when relevant, in order to provide a broader scope of protection. For copper, the lowest of the soil ingestion guideline, the inhalation of indoor air check, the off-site migration check, and groundwater for drinking water check is recommended as the SQG_{HH}.

Therefore, the SQG_{HH}s for agricultural, residential/ parkland, and commercial land uses are based on the soil ingestion guidelines. For industrial land use, the SQG_{HH} is based on the off-site migration check (Table 2).

Soil Quality Guidelines for Copper

The soil quality guidelines are the lower of the SQG_{HH} and SQG_E. For all land uses, the soil quality guideline is the soil concentration calculated for the SQG_E, which is based on the soil contact guideline (Table 1).

Because there are sufficient data to derive an SQG_{HH} and an SQG_E for each land use, the soil quality guideline represents a fully integrated de novo guideline for each land use, derived according to the soil protocol (CCME 1996b) The interim soil quality criteria (CCME 1991) for copper are superseded by the soil quality guidelines.

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 total copper (mg·kg^{-1}).

	Land use			
	Agricultural	**Residential/ parkland**	**Commercial**	**Industrial**
Guideline	**63[a]**	**63[a]**	**91[a]**	**91[a]**
Human health guidelines/check values				
SQG_{HH}	1100[b]	1100[b]	4000[b]	16 000[b]
Soil ingestion guideline	1100	1100	4000	20 000
Inhalation of indoor air check	NC[c]	NC[c]	NC[c]	NC[c]
Off-site migration check	—	—	—	16 000
Groundwater check (drinking water)	NC[d]	NC[d]	NC[d]	NC[d]
Produce, meat, and milk check	NC[e]	NC[e]	—	—
Provisional SQG_{HH}	NC[f]	NC[f]	NC[f]	NC[f]
Limiting pathway for provisional SQG_{HH}	ND	ND	ND	ND
Environmental health guidelines/check values				
SQG_E	63[g]	63[g]	91[g]	91[g]
Soil contact guideline	63	63	91	91
Soil and food ingestion guideline	300	—	—	—
Nutrient and energy cycling check	350	350	350	350
Off-site migration check	—	—	—	610
Groundwater check (aquatic life)	NC[d]	NC[d]	NC[d]	NC[d]
Provisional SQG_E	NC[h]	NC[h]	NC[h]	NC[h]
Limiting pathway for provisional SQG_E	ND	ND	ND	ND
Interim soil quality criterion (CCME 1991)	150	100	500	500

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.

[a]Data 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 1996b). The corresponding interim soil quality criterion (CCME 1991) is superseded by the soil quality guideline.

[b]The SQG_{HH} is the lowest of the human health guidelines and check values.

[c]Applies only to volatile organic compounds and is not calculated for metal contaminants.

[d]Applies to organic compounds and is not calculated for metal contaminants.

[e]Applies to nonpolar organic compounds and is not calculated for metal contaminants.

[f]Because data are sufficient and adequate to calculate an SQG_{HH} guideline for this land use, a provisional SQG_{HH} guideline is not calculated.

[g]The SQG_E is based on the soil contact guideline value.

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

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This fact sheet was originally published in the working document entitled “Recommended Canadian Soil Quality Guidelines” (Canadian Council of Ministers of the Environment, March 1997, Winnipeg). A revised and edited version is presented here.

Reference listing:

Canadian Council of Ministers of the Environment. 1999. Canadian soil quality guidelines for the protection of environmental and human health: Copper (1999). In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.

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

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