

This fact sheet provides Canadian soil quality guidelines for inorganic arsenic (As) for the protection of environmental and human health (Table 1). A supporting scientific document is also available (Environment Canada 1996).

# **Background Information**

Arsenic (CAS 7440-38-2) is a metalloid of the Group 5A elements and exhibits both metallic and nonmetallic properties. The atomic number and atomic weight of arsenic are 33 and 74.92, respectively. Chemically, arsenic closely resembles phosphorus. Arsenic can occur in four oxidation states as arsine (-3), arsenic metal (0), arsenite (+3), and arsenate (+5). Arsenic bonds covalently with most nonmetals and metals. It forms stable organic compounds in both its trivalent and pentavalent states. Arsenic is rarely

found in its elemental form and occurs most commonly as sulphides and as complexes with iron, nickel, copper, and cobalt. The anthropogenic form of arsenic most frequently released to the environment is As(III) oxide.

Arsenic occurs as a minor constituent in complex ores that are mined primarily for their copper, lead, zinc, silver, and gold content. In Canada, gold ores are the main source of arsenic, whereas worldwide, copper ore is the predominant source. Arsenic is usually recovered from dusts and residues associated with the roasting of these ores. It is collected as impure arsenic trioxide and is either purified on site or sold directly to a refiner. Ninety-six percent of arsenic is used as arsenic trioxide or other arsenic compounds; only 4% is used in the metallic state. Demand for arsenic has fallen sharply since the early 1980s because of concerns about environmental effects (Ignatow et al. 1991).

Table 1. Soil quality guidelines for inorganic arsenic (mg·kg<sup>-1</sup>).

	Land use				
	Agricultural	Residential/ parkland	Commercial	Industrial	
Guideline	12 <sup>a</sup>	<b>12</b> <sup>a</sup>	<b>12</b> <sup>a</sup>	<b>12</b> <sup>a</sup>	
SQG <sub>HH</sub>	12	12	12	12	
Limiting pathway for SQG <sub>HH</sub>	Soil ingestion	Soil ingestion	Soil ingestion	Soil ingestion	
Provisional SQG <sub>HH</sub>	NC <sup>b</sup>	NC <sup>b</sup>	NC <sup>b</sup>	NC <sup>b</sup>	
Limiting pathway for provisional SQG <sub>HH</sub>	ND	ND	ND	ND	
$SQG_E$	17	17	26	26	
Limiting pathway for $SQG_E$	Soil contact	Soil contact	Soil contact	Soil contact	
Provisional $SQG_E$	NC <sup>c</sup>	NC <sup>c</sup>	NC <sup>c</sup>	NC <sup>c</sup>	
Limiting pathway for provisional $SQG_E$	ND	ND	ND	ND	
Interim soil quality criterion (CCME 1991)	20	30	50	50	

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

<sup>a</sup>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 1996a). The corresponding interim soil quality criterion (CCME 1991) is superseded by the soil quality guideline.

<sup>b</sup>Because data are sufficient and adequate to calculate an SQG<sub>HH</sub> for this land use, a provisional SQG<sub>HH</sub> is not calculated.

<sup>C</sup>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.

At present in Canada, arsenic is used mainly in metallurgical applications (Environment Canada 1996) and in the manufacture of wood preservatives. Base metal and gold production facilities, the use of arsenical pesticides, coal-fired power generation, and the disposal of domestic and industrial wastes are the principal anthropogenic sources of arsenic release into the Canadian environment. Most (80%) of the anthropogenic releases to the environment are ultimately released to soil (ATSDR 1993). Arsenic is present naturally in the aquatic and terrestrial environments from the weathering and eroding of rock and soil. In areas of arsenic-enriched bedrock. background concentrations can be significantly elevated. Arsenic is released naturally into the atmosphere by volcanic eruptions and the escape of volatile methyl arsines from soil (Chilvers and Peterson 1987).

Mean concentrations of arsenic in several uncontaminated soil types in Canada were reported to range from 4.8 to  $13.6 \,\mu g \cdot g^{-1}$  dw (Kabata-Pendias and Pendias 1992). Data from recent surveys undertaken by the Geological Survey of Canada demonstrate that the "natural background" concentrations of arsenic in surficial media such as glacial tills (the substrate on which most Canadian soils are developed) span several orders of magnitude, reflecting changes in the bedrock geology and the effects of glacial erosion of bedrock debris (I. Kettles 1995, Natural Resources Canada, pers. com.). Concentrations of arsenic in glacial till samples from a number of Canadian sites range from 1 to  $6590 \,\mu g \cdot g^{-1}$  dw. Average urban and agricultural concentrations are at or below  $10 \,\mu g \cdot g^{-1}$  dry soil, with most of the values in the 4–6  $\mu g \cdot g^{-1}$  range (Environment Canada 1996).

In surface soil samples from areas not impacted by local point sources of pollution throughout Ontario, the 98th percentiles of arsenic concentration measurements are 11 and 17 mg·kg<sup>-1</sup> for rural parkland and old urban parkland soils, respectively (OMEE 1993).

Canadian drinking water supplies usually contain  $<5 \ \mu g \ As \cdot L^{-1}$ , primarily as As(V), but higher levels of inorganic arsenic as both As(III) and As(V) are normally found in groundwater, especially in areas with natural geological sources. Low mean concentrations of arsenic in PM10, 0.001  $\ \mu g \cdot m^{-3}$ , have been reported in ambient air masses over major Canadian urban centres for a number of years. Average concentrations of total arsenic in foods are generally in the low nanogram per gram range, but in marine fish, concentrations may exceed 3000 ng·g<sup>-1</sup>. Limited data show that the percentage of inorganic arsenic in foods ranges from 0% in marine fish to 75% in dairy products, beef, and pork, with the remainder present in essentially nontoxic organic forms (Environment Canada 1996).

The analytical method recommended for arsenic by the CCME is the U.S. EPA Method 6010 (inductively coupled plasma-atomic emission spectroscopy) (CCME 1993a, 1993b). Following corrections for a 1-g soil sample, digested, with the final extract being diluted to 100 mL, a detection limit of 5.3 mg·kg<sup>-1</sup> for arsenic would be calculated.

# **Environmental Fate and Behaviour in Soil**

Many factors control the fate and behaviour of arsenic in soil and, ultimately, its bioavailability. It is generally accepted that only soluble arsenic is available for plant uptake. The solubility and speciation of arsenic in solution are primarily determined by pH and the reduction/oxidation potential. The solubility of arsenic may determine the amount of arsenic ultimately available within a system, while the speciation of arsenic determines the behaviour and, to a large extent, the toxicity of arsenic.

Generally, in oxidizing conditions or aerobic soils, inorganic arsenic is predominantly present as arsenate,  $AsO_4^{3-}$ , with arsenic in the +5 oxidation state. Thermodynamically,  $H_2AsO_4^{-}$  is the most stable species between pH 2 and pH 7. Above pH 7,  $HAsO_4^{2-}$  is the most stable species.

Under reducing conditions, as in anaerobic, water-logged soils, arsenic is primarily present as arsenite,  $AsO_3^{3-}$ , with arsenic in the +3 oxidation state.  $H_3AsO_3$  is thermodynamically the most stable species up to about pH 9 and is the predominant species within the normal soil pH range. Under strongly reduced conditions, elemental arsenic and arsine (AsH<sub>3</sub>) can exist.

A variety of microorganisms can methylate arsenic. Methylated arsenic oxyacids are found in various natural waters, soils, and sediments (Masscheleyn et al. 1991).

One of the most important processes influencing the behaviour and bioavailability of arsenic in soil is its ability to sorb onto solids or particulates. Soil sorption controls the persistence, activity, and movement of arsenic species. Factors governing the sorption of arsenic in soil include pH and the amount of clay, iron, aluminum, calcium, and phosphorus present.

The pH influences the distribution of arsenic species present in solution and activates the anion adsorption sites on clay minerals, thus affecting adsorption. At low pH, hydroxyl groups exposed on the periphery of metal oxides, clay minerals, and amorphous silicate minerals are protonated and acquire a positive charge. These protonated (activated) sites are then available for the interaction and adsorption of the arsenical anions present in solution (Sposito 1989).

Arsenic is strongly adsorbed by clay minerals such as kaolinite, limonite, montmorillonite, and vermiculite (Dickens and Hiltbold 1967; Slooff et al. 1990). Arsenic can be strongly sorbed to electropositive hydroxides such as aluminum, iron, and calcium, which coat clay particles or react with cations in the soil solution (Jacobs et al. 1970).

Soil solutions contain several different constituents capable of competing for adsorption sites (Roy et al. 1986), particularly phosphorus, selenium, and molybdate. Arsenic and phosphorus are chemically similar and exist as oxyanions, which may compete for fixation sites in soil and for uptake in plants (Woolson 1973; Asher and Reay 1979).

Inorganic arsenic is more mobile than organic arsenic in soil, and arsenite is more mobile than arsenate (Xu et al. 1988). Thus, inorganic arsenic and arsenite might leach into surface waters and groundwaters (NRCC 1978). Despite the relative stability of soluble ionic species, concentrations of arsenicals in pore waters are usually low (O'Neill 1990). It seems that adsorption dominates the partitioning of arsenic to the particulate phase, hence leaching of arsenicals at greater soil depths is well correlated with the decreasing adsorptive capacities of the soil. Essentially, leaching occurs when arsenical application rates exceed the adsorption capacity of the soil. Leaching is pronounced in sandy soils and soils lacking in hydroxides of iron, aluminum, and calcium (Woolson et al. 1971).

# **Behaviour and Effects in Biota**

## Soil Microbial Processes

Studies reporting exposures to inorganic forms of arsenic have shown that As(III) oxide will produce inhibitory effects on normal urease activity in selected soils, but that the degree of inhibition is dependent on soil type (Tabatabai 1977). Other studies have shown than As(III) is a more effective inhibitor of urease and amidase activity and nitrification than As(V) (Tabatabai 1977; Liang and Tabatabai 1977; Frankenberger and Tabatabai 1981). The opposite effect on acid and alkaline phosphatase activity is evident, with As(V) causing greater inhibition of activity (Juma and Tabatabai 1977). Neither As(III) or As(V) was shown to strongly inhibit nitrogen mineralization (Liang and Tabatabai 1977).

## Terrestrial Plants

Arsenic uptake and its subsequent translocation can be influenced by plant species, the chemical form of arsenic, and temperature. Though plants grown in arsenic-treated soil may contain considerably greater concentrations of arsenic than plants grown in untreated soils, terrestrial plants rarely contain higher concentrations of arsenic than their substrate.

The lowest concentration of arsenic in soil at which phytotoxic effects have been observed is 10 mg·kg<sup>-1</sup>, which resulted in yield reductions of 22 and 42% in green beans, 33 and 41% in spinach, and 17 and 23% in radishes, depending on soil type. Yield reductions of 26% in cabbage and 22% in lima beans were also observed at 10 mg As·kg<sup>-1</sup> soil (Woolson 1973). In the same study, tomatoes were not affected at 100 mg As·kg<sup>-1</sup> soil.

## Terrestrial Invertebrates

An experiment by Beyer and Cromartie (1987) reporting arsenic concentrations in earthworms from 20 different contaminated and uncontaminated sites indicated that arsenic does not bioaccumulate to any appreciable degree.

The lowest arsenic concentration at which adverse effects were observed (using soil as the test medium) is 100 mg·kg<sup>-1</sup>, which resulted in 50% mortality of earthworms (*Eisenia foetida*). The earthworms were not affected at 83 mg·kg<sup>-1</sup> (Environment Canada 1995).

# Livestock and Wildlife

Terrestrial mammal populations may be exposed to various forms of arsenic through inhalation of aerosols or ingestion of particulate-adsorbed arsenicals. Uptake of arsenic through ingestion of contaminated forage is not an important route of exposure because concentrations of arsenic in terrestrial plants are generally low. However, direct ingestion of arsenic from soil can be a major source of dietary arsenic for grazing livestock. The amount of soilbound arsenic ingested can account for 60–75% of total arsenic intake in cattle. Only about 1% of this is actually absorbed, with the remainder being excreted directly.

The lowest reported  $LD_{50}$  in terrestrial mammals is  $8 \text{ mg} \cdot \text{kg}^{-1}$  bw per day for rabbits; for birds it is 47.6 mg \cdot \text{kg}^{-1} bw per day.

# Human and Experimental Animal Health Effects

The general Canadian population is exposed to inorganic arsenic in ambient air, drinking water, soil, and food. Estimates of total daily intake of inorganic arsenic range from 0.18 to 0.73  $\mu$ g·kg<sup>-1</sup> bw per day for adults and infants

fed a mixed diet, respectively. Drinking water and food constitute the main sources of inorganic arsenic exposure for all age classes of the general population and together account, in nearly equal proportions, for 92–98% of the total daily intake. About 2% of the total daily exposure to inorganic arsenic is from soil/dust ingestion for most age classes. However, infants and young children sustain a greater exposure via soil/dust ingestion (4 and 9% of total daily intake, respectively). With the exception of smokers, exposure to inorganic arsenic by inhalation is insignificant for the general population.

Inorganic arsenic is the form of primary toxicological concern in humans. Elemental arsenic and organic arsenic compounds are considered less toxic in humans and laboratory animals than inorganic forms, but this is not well documented. Soluble inorganic arsenic compounds (trivalent and pentavalent) are readily and almost completely absorbed from the gastrointestinal tract. Absorbed inorganic arsenic is stored mainly in the liver, kidneys, lungs, spleen, and skin. As(III) is detoxified in the liver by enzymatic methylation, and the methylated by-products are quickly eliminated in the urine. For methylation to occur, As(V) must be first reduced to As(III). The absorption of other forms of arsenic may vary considerably. Elemental arsenic is poorly absorbed, while organic arsenic compounds are well absorbed, but both these forms are largely and rapidly eliminated unchanged from the human body and thus are not considered as toxic as inorganic arsenic compounds. Inorganic arsenic compounds have been consistently demonstrated in numerous studies to cause cancer in humans exposed by both inhalation and ingestion. On this basis, Health and Welfare Canada (1992) and Government of Canada (1993) have classified "the group of inorganic arsenic compounds as a whole" in Group 1 ("carcinogenic to humans") of the classification scheme developed by the Bureau of Chemical Hazards for use in the derivation of the Guidelines for Canadian Drinking Water Quality (Health and Welfare Canada 1989). The group of inorganic arsenic compounds as a whole is therefore considered to be a nonthreshold toxicant (i.e., a substance for which there is believed to be some chance of adverse health effects at any level of exposure).

Ingestion of inorganic arsenic compounds in drinking water or in medicinals has been repeatedly and strongly associated with skin cancer in human studies. In addition to skin cancer, various cancers of internal organs (including the bladder, kidneys, and lungs) have also been reported in populations exposed to high levels of arsenic in drinking water. Rare tumours of the liver (hepatic angiosarcomas) and lung cancer have also been linked with ingestion of arsenic-containing medicines in some patients. Noncancerous adverse effects on the skin and possibly peripheral vascular diseases (such as black foot disease, a condition leading to gangrene of the toes and feet in a Taiwanese population) have also been reported in human populations chronically exposed to arsenic, although at levels generally associated with an estimated large excess of cancer risks.

# **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 for arsenic soil quality guidelines are provided in Environment Canada (1996).

# Soil Quality Guidelines for Environmental Health

Environmental soil quality guidelines (SQG<sub>E</sub>s) are based on soil contact using data from toxicity studies on plants and invertebrates. In the case of agricultural land, 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  $SQG_E$ .

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 arsenic, there are insufficient data to derive a nutrient and energy cycling check, and the soil contact guidelines are recommended as the  $SQG_E$  for all land uses (Table 2).

	Land use				
	Agricultural	Residential/ parkland	Commercial	Industrial	
Guideline	<b>12</b> <sup>a</sup>	<b>12</b> <sup>a</sup>	12 <sup>a</sup>	<b>12</b> <sup>a</sup>	
Human health guidelines/check values					
SQG <sub>HH</sub>	12 <sup>b</sup>	12 <sup>b</sup>	12 <sup>b</sup>	12 <sup>b</sup>	
Soil ingestion guideline	12	12	12	12	
Inhalation of indoor air check	NC <sup>c</sup>	NC <sup>c</sup>	NC <sup>c</sup>	NC <sup>c</sup>	
Off-site migration check	—	—		39	
Groundwater check (drinking water)	NC <sup>d</sup>	NC <sup>d</sup>	NC <sup>d</sup>	NC <sup>d</sup>	
Produce, meat, and milk check	NC <sup>e</sup>	NC <sup>e</sup>	_	_	
Provisional SQG <sub>HH</sub> Limiting pathway for provisional SQG <sub>HH</sub>	NC <sup>f</sup> ND	NC <sup>f</sup> ND	NC <sup>f</sup> ND	NC <sup>f</sup> ND	
Environmental health guidelines/check values					
SQG <sub>E</sub>	17g	17 <sup>g</sup>	26 <sup>g</sup>	26 <sup>g</sup>	
Soil contact guideline	17	17	26	26	
Soil and food ingestion guideline	380		—		
Nutrient and energy cycling check	NC <sup>h</sup>	NC <sup>h</sup>	NC <sup>h</sup>	NC <sup>h</sup>	
Off-site migration check	—	—		140	
Groundwater check (aquatic life)	NC <sup>d</sup>	NC <sup>d</sup>	NC <sup>d</sup>	NC <sup>d</sup>	
Provisional SQG <sub>E</sub> Limiting pathway for provisional SQG <sub>E</sub>	NC <sup>i</sup> ND	NC <sup>i</sup> ND	NC <sup>i</sup> ND	NC <sup>i</sup> ND	
Interim soil quality criterion (CCME 1991)	20	30	50	50	

Table 2. Soil quality guidelines and check values for inorganic arsenic (mg·kg<sup>-1</sup>).

**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.

<sup>a</sup>Data are sufficient and adequate to calculate an SQG<sub>HH</sub> and an SQG<sub>E</sub>. 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.

<sup>b</sup>The SQG<sub>HH</sub> is the lowest of the human health guidelines and check values.

<sup>c</sup>Applies only to volatile organic compounds and is not calculated for metal contaminants.

<sup>d</sup>Applies to organic compounds and is not calculated for metal contaminants. Concerns about metal contaminants should be addressed on a sitespecific basis.

<sup>e</sup>Applies to nonpolar organic compounds and is not calculated for metal contaminants. Concerns about metal contaminants should be addressed on a site-specific basis.

<sup>f</sup>Because data are sufficient and adequate to calculate an SQG<sub>HH</sub> for this land use, a provisional SQG<sub>HH</sub> is not calculated.

 $^{g}$ The SQG<sub>E</sub> is based on the soil contact guideline value.

<sup>h</sup>Data are insufficient/inadequate to calculate the nutrient and energy cycling check for this land use.

<sup>i</sup>Because data are sufficient and adequate to calculate an SQG<sub>E</sub> for this land use, a provisional SQG<sub>E</sub> is not calculated.

#### Soil Quality Guidelines for Human Health

Human health soil quality guidelines (SQG<sub>HH</sub>s) for nonthreshold (carcinogenic) contaminants require the development of soil quality guidelines that employ a critical risk-specific dose based on lifetime incremental risks from soil ingestion. For all land uses, the adult was chosen as the receptor when considering lifetime cancer risk. For nonthreshold contaminants, human exposure should be reduced to the maximum extent possible. Consequently, lifetime incremental risks of  $10^{-4}$  to  $10^{-7}$  above background are provided by Health Canada as soil quality guidelines for all land uses (Environment Canada 1996).

The CCME Subcommittee on Environmental Quality Criteria for Contaminated Sites recommends a human health soil quality guideline based on an incremental risk from exposure of  $10^{-6}$  (CCME 1996a). It should be noted that the  $10^{-6}$  incremental risk above background falls within the range (< $10^{-5}$  to  $10^{-6}$ ) considered to be "essentially negligible" in the derivation of MACs for carcinogenic chemicals in drinking water (Health and Welfare Canada 1989).

The highest reported mean background concentration for inorganic arsenic came from urban environments not directly impacted by point sources, and was 10  $\mu$ g·g<sup>-1</sup> of dry soil, which is below the proposed guideline. However, it is possible that the incremental risk-specific guidelines for residential/parkland and industrial land uses may be below soil background levels in some areas of Canada. Where local or regional background soil concentrations of arsenic differ markedly from 10  $\mu$ g·g<sup>-1</sup>, then site-or region-specific guidelines should be derived, incorporating the local/regional background soil concentrations.

Various check mechanisms are applied, if relevant, to the human health soil ingestion guidelines in order to provide them with a broader scope of protection. The only human health check value calculated for arsenic is the off-site migration check for industrial land use. The lower of the off-site migration check value and the soil ingestion guideline is recommended as the SQG<sub>HH</sub> for industrial land use. Therefore, the soil ingestion guidelines are recommended as the SQG<sub>HH</sub> for all land uses (Table 2).

## **Soil Quality Guidelines for Arsenic**

The soil quality guidelines are the lower of the  $SQG_{HH}$  and  $SQG_{E}$ . For all land uses, the guideline is the soil concentration calculated for the  $SQG_{HH}$ , which is based on soil ingestion of a nonthreshold substance (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 1996a). The interim soil quality criteria for arsenic (CCME 1991) are superseded by the soil quality guidelines.

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

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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.

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