

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

Barium 2013

his summary provides Canadian soil quality guidelines for barium for the protection of environmental and human health (Table 1). A supporting scientific document is also available for human health and environmental health (CCME 2012; EC 1999).

## **Background Information**

Barium (CAS 7440-39-3) is an alkaline-earth metal (Group IIA of the periodic table) that is silver-white in appearance with an atomic number of 56 and a relative molecular mass of 137.33. Although 25 barium isotopes have been identified (WHO 1990), barium occurs as a mixture of 7 stable isotopes with weights of 130, 132, 134, 135, 135, 137 and 138 and abundances (as %) of 0.101, 0.097, 2.42, 6.59, 7.81, 11.32 and 71.66, respectively (Boffito 1991).

Barium readily oxidises in air and reacts with water; in nature it occurs as a divalent cation combined with other elements (CICAD 2001). At room temperature, it combines readily, and exothermically, with oxygen and the halogens and reacts explosively with water to form barium hydroxide (Ba(OH)<sub>2</sub>). At elevated temperatures, it reacts with hydrogen to form barium hydride (BaH<sub>2</sub>) and nitrogen to form barium nitride (Ba<sub>3</sub>N<sub>2</sub>) (Boffito 1991).

The barium salts of acetate, hydroxide, silicate, chlorate, nitrate, thiocyanate, cyanide, oxide and halide are soluble in water. The salts of arsenate, carbonate, citrate, fluoride, oxalate, and tartrate are sparingly soluble in water but soluble in acids. Barium chromate and phosphate are insoluble in water, but soluble in acids whereas barium

	Land Use				
	Agricultural	Residential/ Parkland	Commercial	Industrial	
Guideline	<b>750</b> <sup>a</sup>	<b>500</b> <sup>a</sup>	<b>2000</b> <sup>a</sup>	<b>2000</b> <sup>a</sup>	
SQG <sub>HH</sub> Limiting pathway for SQG <sub>HH</sub>	6800 Direct contact	6800 Direct contact	10 000 Direct contact	96 000 Offsite migration	
Provisional SQG <sub>HH</sub> Limiting Pathway for provisional SQG <sub>HH</sub>	ND <sup>b</sup> ND	ND <sup>b</sup> ND	ND <sup>b</sup> ND	ND <sup>b</sup> ND	
SQG <sub>E</sub> Limiting Pathway for SQG <sub>E</sub>	NC <sup>c</sup> ND	NC <sup>c</sup> ND	NC <sup>c</sup> ND	NC <sup>c</sup> ND	
Provisional SQG <sub>E</sub> Limiting Pathway for Provisional SQG <sub>E</sub>	NC <sup>c</sup> ND	NC <sup>c</sup> ND	NC <sup>c</sup> ND	NC <sup>c</sup> ND	
1999 Barium Soil Quality Guideline (CCME 1999)	750	500	2000	2000	
Interim Soil Quality Criterion (CCME 1991)	750	500	2000	2000	

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

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

<sup>a</sup>Data are sufficient and adequate to calculate only a SQG<sub>HH</sub>. It is greater than the corresponding interim soil quality criteria (CCME 1991). Therefore the interim soil quality criterion (and 1999 soil quality guideline) is retained as the soil quality guideline for this land use.

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

<sup>c</sup>Data are insufficient/inadequate to calculate an SQG<sub>E</sub>, or provisional SQG<sub>E</sub> for this land use.

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. Use of some values listed in Table 1 may not be permitted at the generic level in some jurisdictions. The reader should consult the appropriate jurisdiction before application of the values.

sulphate is insoluble in water and only sparingly soluble in acids, requiring strong  $H_2SO_4$  to dissolve. All barium salts, except sulphate, exhibit increasing solubility with decreasing pH (WHO 1990).

Barium combines with most metals to form a wide range of alloys and intermetallic compounds. Many barium compounds are readily reduced by Mg and Ca to produce barium alloys (Boffito 1991).

Organometallic compounds of barium are ionic and readily hydrolyse in water. Barium will form weak complex compounds with chloride, hydroxide and nitrate anions that contribute very little to total barium concentrations.

Barium complex formation does not readily occur. The amines formed are unstable and the  $\beta$ -diketones and alcoholates are not well characterised (WHO 1990).

Barium has been identified in over 80 minerals but is never found as a free metal in nature (DiBello *et al.* 1991). It only occurs in significant quantities in barite (BaSO<sub>4</sub>) and witherite (BaCO<sub>3</sub>) (Boffito 1991; DiBello *et al.* 1991).

Barite deposits have been found in all provinces except Alberta, Saskatchewan and Prince Edward Island. More than 150 deposits have been identified in Canada, many of them are small and of low commercial interest. However, some have been developed into producing mines. There are four main barite orebodies in Canada. These include: the Walton orebody in Nova Scotia; the Giant Mascot and Mineral King orebodies in British Columbia; and the Buchans orebody in Newfoundland and Labrador (Dumont 2007).

The global barite production for 2006 was estimated to be over 7.9 Mtonnes (Mt) with China (4.4 Mt), India (1.0 Mt) and the United States (589 000 t) leading the production. Canadian production of barite and witherite in 2007 was estimated at close to 7196 t which is down from 19 597 t in 1996 (Dumont 2007). However, Dumont (2007) estimated 68 971 t of barite and witherite were used in Canada in 2007 (approximately 62 172 t were imported).

Barium minerals and compounds are widely used in a number of key industries and generally the physical and chemical properties of the raw mineral determine its destination. More than 90% of the barium used is in the form of barite ore after preliminary beneficiation (DiBello *et al.* 1991). Globally, 85% of barite is used as a drilling fluid additive, 10% is used in the chemical sector and 5% as fillers (Dumont 2007).

Barite is present as a filler and extender in paints, plastics and rubber products as it imparts several desirable qualities to these products. Barite acts as a heat sink in clutch pads and brake linings. In the manufacture of glass and ceramics it is used as a flux. Other uses include product manufacturing (bowling balls, ink, oilcloth, photographic paper, artificial ivory, cellophane, wallpaper, adhesives, sealants, and polymeric fibres and resins); sugar refining; metal casting; chocolate manufacturing; heavy concrete production; firework production and pond repair (AENV 2004).

In addition, barite is used as a feedstock for the production of other barium chemicals. Because of its high density and low solubility and toxicity, BaSO<sub>4</sub> is used in X-ray diagnostic tests (DiBello *et al.* 1991; NRCan 2003, AENV 2004). Barium carbonate (produced through thermal reduction) is used in the manufacture of glass, clay and brick products. Some BaCO<sub>3</sub> is also used in the manufacture of barium ferrites (DiBello *et al.* 1991).

Barium hydroxide is used in sugar refining, waterproofing and fire-proofing of sizings and coatings, the manufacture of polyurethane foams and as a plastics stabiliser. Barium nitrate is used in the production of green flares and tracer bullets (DiBello *et al.* 1991).

Barium metal produced from barium carbonate is used to remove gas traces from vacuum and television picture tubes. It is also used to improve the performance of lead alloy grids of acid batteries, as a lubricant in vacuum Xray tubes and as a component in various nodulising and deoxidising alloys (Boffito 1991). Barium is also used in the production of agricultural insecticides, rodenticides, herbicides and germicides and in the manufacturing of pharmaceutical products such as vitamins, blood coagulants, hormones and cosmetics (Reeves 1986).

Barium alloys are used in iron production to control the shape of nodular graphite inclusions and as reducing agents, to remove oxygen from molten steel, copper and other metals.

Organometallic barium compounds are currently used to reduce black smoke emissions from diesel fuels (Miner 1969; WHO 1990).

Data on barium concentrations in air were provided by Environment Canada from the National Air Pollution Surveillance (NAPS) network (Environment Canada 2011). The mean barium concentrations in ambient air (PM<sub>2.5</sub>) analysed by ICP-MS following acid digestion is  $1.9 \text{ ng/m}^3$  (arithmetic mean, SD=3.2, n=3054) (Health Canada 2011). This is based on 2003-2009 NAPS data collected from urban and rural locations in British Columbia, Ontario, Québec and New Brunswick (data are not currently available for other provinces and territories).

The background barium concentration in indoor air was determined to be 2.7  $ng/m^3$  (arithmetic mean, SD=4.2, n=40) based on two North American studies, Alberta Health (1998) and Graney *et al.* (2003) (Health Canada 2011).

Metal content in house dust and garden soils from 10 zones in the City of Ottawa was determined by ICP-MS; the barium detection limit was 1 mg/kg. A wide range of barium concentrations were reported in house dust (n=48), from 190 to 1480 mg/kg with a mean of 492 mg/kg and a median of 454 mg/kg (dry weight) (Rasmussen *et al.* 2001). Based on this Canadian study and the NHEXAS (National Human Exposure Assessment Survey) database (US EPA 2009), the background concentration in Canadian indoor dust was determined to be 305.3 mg/kg (arithmetic mean, SD=311.3, n=165).

Barium is ubiquitous in soils with concentrations ranging from 15 to 3000 mg/kg (ATSDR 1992). However, near barite deposits soil barium concentrations can be as high as 37 000 mg/kg (Adriano 1986). The Geological Survey of Canada (GSC) houses a large geochemical background soil database which was used to develop the background concentration of barium in soil for Canada. It is acknowledged that barium concentrations in soil throughout Canada will vary based on geology and anthropogenic inputs; however, a single background soil concentration is required to develop soil quality guidelines for use throughout Canada. The mean concentration of barium in Canadian soil is 140 mg/kg (arithmetic mean, SD=120, n=7397) (Grunsky 2010). This value is based on GSC data obtained from till samples (<63µm) that were analysed by AAS/ICP-ES following aqua-regia digestion (partial digestion by HCl and HNO<sub>3</sub>). These samples were obtained from Newfoundland and Labrador, New Brunswick, Québec, Nunavut, Northwest Territories, Manitoba, Saskatchewan, Alberta and British Columbia.

Anthropogenic discharges into water occur during barium ore processing and subsequent industrial chemical processes involving barium (WHO 1990; ATSDR 1992). Barium emissions into water have also been reported during coal processing. The effluent from a coal conversion plant was reported by Hildebrand *et al.* (1976) to contain 20 µg Ba/L.

High levels of barium can be found in groundwater due to leaching and eroding of barium from sedimentary rocks (WHO 1990) and coal. Groundwater at a proposed coal mine site in British Columbia. was reported to contain 1200 to 10 800  $\mu$ g Ba/L with a mean value of 7300  $\mu$ g Ba/L (Buchanan 1985).

The background barium concentration in Canadian drinking water is 34.2  $\mu$ g/L (arithmetic mean, SD=68.6, n=14 144) based on data obtained from the Ontario Ministry of Environment (1998-2007), Saskatchewan Ministry of Environment (2000-2009) and Department of Environment and Conservation, Government of Newfoundland and Labrador (2000-2009) (Health Canada 2011). Data from other provinces and territories were not available for the estimation of a national average.

The barium concentration in human breast milk was determined to be 3.61  $\mu$ g/L (arithmetic mean, SD=8.67, n=495) (Health Canada 2011). This concentration includes breast milk at various stages/maturity.

Health Canada's Food Directorate has provided estimated daily intakes of barium from food in Canadians from the Health Canada Total Diet Study (HC TDS) (Dabeka *et al.* 2010). Intake rates were provided for various age groups from 2000 to 2007 (inclusive) as presented in the table below.

Estimated Daily Intakes of Barium from Food for Canadians (HC TDS)

(µg/kg-d)	0-6m	7m- 4y	5-11y	12- 19y	20+y
	M&F	M&F	M&F	M&F	M&F
arithmetic mean	19	21	16	9.1	7.0
standard deviation	3.0	2.5	1.8	1.1	1.1

## **Environmental Fate and Behaviour in Soil**

No current release estimates were identified for Canada, however, 1998 release estimates for barium compounds from U.S. manufacturing and processing facilities were 900 tonnes to air, 45 tonnes to water, and 9300 tonnes to soil (CICAD 2001).

In air, barium is associated with dust and suspended particulates. Barium occurs mainly as the sulphate and carbonate and possibly as other insoluble forms (WHO 1990; ATDSR 2007). Depending on the particle size the residence time of barium in the atmosphere may be several days with larger particles settling out more quickly (CICAD 2001). Barium compounds in

#### BARIUM

particulates are likely removed from the atmosphere by wet and dry deposition (HSDB 2003).

Barium concentrations in water are determined by the solubility of barium salts and the adsorption of barium on active surfaces. Soluble barium compounds are mobile in the environment and have been detected in surface water, groundwater, drinking water, and sediment (HSDB 2003). Aqueous environments containing chloride, nitrate and carbonate anions will increase the solubility of barium sulfate and at a pH 9.3 or less, the Ba(II) ion will be the dominant species and will be controlled by the sulphate ion concentration (ATSDR 2007). Natural (i.e. surface water) and treated (i.e. drinking water) waters generally contain sufficient sulphate to limit Ba(II) concentrations to <1500 mg/L (ATSDR 2007). At pH levels >9.3, barium carbonate becomes the dominant species and limits Ba (II) solubility (Bodek et al. 1988). The barium concentration in water has been reported to be related to the water hardness, defined as the sum of the polyvalent cations present, including Ca, Mg, Fe, Mn, Cu, Ba and Zn ions (NAS 1977).

Barium is capable of adsorption onto clays, manganese oxides and zeolite minerals and is found to occur in deepsea manganese nodules and freshwater manganese deposits. Ferromanganese nodules found on the ocean floor are reported to be one of the major barium sinks (Adriano 1986). The increase in barium concentrations in the marine environment with increased depth may be due to the incorporation of barium into organisms in the euphotic zone and subsequent sedimentation and release into deeper waters (CICAD 2001).

Barium occurs naturally in soils with high levels associated with limestone, feldspar and shale deposits (WHO 1990). Weathered, soluble barium minerals in solution may come in contact with sulphate solutions and deposit in geological faults as BaSO<sub>4</sub>. However, if insufficient sulphate is present, the soil material formed will be partially saturated with barium where it may displace other cations in the soil (WHO 1990).

Barium mobility in soils depends on soil characteristics and the solubility of the barium compounds formed (ATSDR 2007; CICAD 2001). Barium is easily precipitated as sulphates and carbonates. Barium reacts readily with metal oxides and hydroxides, being subsequently adsorbed onto soil particles (Rai *et al.* 1984). Barium will displace other adsorbed alkaline earth metals from MnO<sub>2</sub>, SiO<sub>2</sub> and TiO2 (Rai *et al.* 1984) as well as substituting for K(I) (Adriano 1986). In addition, adsorption occurs through electrostatic interactions controlled by the ability of the sorbent to exchange cations (WHO 1990). Barium is strongly adsorbed to clay minerals and organic and fine structured soils (WHO 1990; ATSDR 2007). Generally barium shows limited mobility because of the formation of water insoluble salts and the inability of barium to form soluble humic and fulvic complexes (WHO 1990). However, barium may move into groundwater under acidic conditions since the solubility of barium compounds increases with decreasing pH (CICAD 2001; ATSDR 2007). It is noteworthy that the application of lime or sulphur to soil tends to immobilise barium by forming the sparingly soluble BaCO<sub>3</sub> and BaSO<sub>4</sub> (Adriano 1986).

# **Behaviour and Effects in Biota**

### Soil Microbial Processes

No data were available on the effects of barium on soil microorganisms and microbial processes.

### Terrestrial Plants

Barium is found in most plants, although not reported to be essential (WHO 1990). The concentration depends on soil and plant species. Although not thoroughly studied (ATSDR 2007), little barium is bioconcentrated by land plants, (Schroeder 1970, WHO 1990) and no plant uptake from air has been reported (WHO 1990). It is actively and strongly accumulated by legumes, grain stalks, forage plants, red ash, black walnut, hickory and Brazil nut trees, Douglas fir and plants of the genus Astragallu (Reeves 1986; WHO 1990, CICAD 2001). With the exception of the Brazil nut, the parts of the plant that accumulate barium are rarely eaten by humans (WHO 1990). The distribution of barium in plant tissues indicates that the highest levels are found in the roots. In sedge and nutgrass values of 97.6 and 131.9 µg/g (roots), 15.4 and 37.5  $\mu$ g/g (leaves), 10.0 and 11.6  $\mu$ g/g (seeds) and 9.2 and 11.1µg/g (stem) were reported (Cherry and Guthrie 1979), respectively.

Tree foliage sampling data (dry weight basis), to evaluate metal content in airborne deposition, was available for background locations in Ontario and Manitoba. In Ontario, barium was detected in the foliage of silver maple trees (n=63) in rural locations (Essex and Kent counties) at concentrations ranging from 2.4 to 9.5  $\mu$ g/g (dry weight) (Gizyn 2002).

Various terrestrial plants have demonstrated sensitivity to barium. It has been suggested that barium is toxic to plants only in the absence of sufficient calcium (Robinson and Whetstone 1950). Under experimental conditions, bush beans and barley displayed toxicity and accumulated 10-20 mg Ba/g in leaf tissues when grown in soil spiked with 2 mg/g Ba nitrate (Chaudry *et al.* 1977). Davis *et al.* (1978) exposed young spring barley to concentrations of barium chloride in a silver sand and nutrient solution. Barium was toxic only at very high concentrations. Barium chloride solutions gave rise to harmful osmotic effects or chloride toxicity before they were sufficiently concentrated to elicit barium-specific toxicity. In contrast, no difference in barium uptake was found in Swiss chard and ryegrass growing in soils amended with two types of drilling fluids, compared to controls (Nelson *et al.* 1984).

Toxicological tests were performed on radish (*Raphanus sativa*) and lettuce (*Lactuca sativa*) using  $BaCl_2 \cdot H_2O$  in artificial soil (Environment Canada 1996). Results for seedling emergence in lettuce were: NOEC: 177 mg/kg,  $LC_{25:}$  325 mg/kg and  $LC_{50:}$  868 mg/kg. The NOEC,  $LC_{25}$  and  $LC_{50}$  for radish seedlings were 1055 mg/kg, 1064 mg/kg and 2944 mg/kg respectively. The toxic endpoints reported in this test are likely due to the chloride ion rather than the barium ion due to its dissociation in the soil solution (Davis 1972).

### Terrestrial Invertebrates

Although various compounds containing barium have been used as pesticides for the control of certain terrestrial invertebrates (Grace 1990; Grace and Abdallay 1990), little toxicological information specific to barium has been reported in the scientific literature.

Environment Canada (1996) exposed earthworms (*Eisenia foetida*) to concentrations of BaCl<sub>2</sub> in an artificial soil. The reported effect was mortality and the endpoints included a NOEC, LOEC, LC<sub>25</sub> and LC<sub>50</sub> at 2390 mg/kg, 2894 mg/kg, 2952 mg/kg and 3154 mg/kg respectively. The effects observed may also have been attributable to the chloride ion in the soil solution.

### Livestock and Wildlife

In animals, barium tends to be concentrated in the bones where it competes with calcium for exchange sites (Taylor *et al.* 1962).

In mammals, the intestinal mucosa is readily permeable to  $Ba^{+2}$  ions and is involved in the rapid flow of soluble barium salts into and out of the blood. Since barium in food occurs in bound or insoluble forms, absorption is about 2% of the total dietary barium content (Venugopal and Luckey 1978; Reeves 1986). Symptoms of acute barium poisoning in human and other mammals may include excessive salivation, vomiting, colic, violent diarrhea, tremors, muscular paralysis, sever cardiotoxicity

and paralysis of the central nervous system (Venugolal and Luckey 1978).

Borzelleca *et al.* (1988) performed short-term toxicity tests with BaCl<sub>2</sub> on male and female Sprague-Dawleyderived rats by oral gavage. The reported LD<sub>50</sub>s (95% confidence limits) for male and female rats were 419 (352-499) and 408 (342-487) mg BaCl<sub>2</sub>/kg. Tradiff *et al.* (1980) reported an LD<sub>50</sub> of 220 mg/kg body weight for weanlings and 132 mg/kg body weight for adult Charles River rats exposed to barium chloride through drinking water. For chickens, Johnson *et al.* (1960) reported an LD<sub>50</sub> of 623 mg/kg body weight when Ba(OH)<sub>2</sub> was given orally in caplets and a 16% reduction in growth when 2000 mg/kg body weight was administered in the feed.

# Behaviour and Effects in Humans and Nonhuman Mammalian Species

The majority of the toxicity data for barium is based on studies using soluble forms of barium, although the most predominant form of barium found in the environment is insoluble barium sulphate (barite), which is not considered in this SQG.

The toxicity of barium is attributed to the barium ion (Ba+2) and therefore, the toxicity of a particular barium compound is related to that compound's solubility (ATSDR 2007; US EPA 2005; CICAD 2001). The intestinal mucosa of mammals is highly permeable to barium ions which are readily absorbed from the gastrointestinal tract and lung. Soluble barium salts move rapidly into the blood (DiBello *et al.* 1991).

The mechanism of barium toxicity is related to its ability to substitute for calcium. Toxicity results from stimulation of smooth muscles of the gastrointestinal tract, the cardiac muscle, and the voluntary muscles, resulting in paralysis (DiBello *et al.* 1991). Toxicity can also result from barium acting as a physiological antagonist to potassium ions, which possess a similar effective ionic radius. Hypokalemia is associated with the ability of barium ions to block potassium channels (Koch *et al.* 2003).

The intentional or accidental ingestion of soluble barium compounds can result in acute barium toxicity. Systemic effects of barium toxicity include abdominal pain, nausea, vomiting and diarrhea, hypertension, cardiac arrhythmias, muscle paralysis and death. (US EPA 2005; Jourdan *et al.* 2003; Koch *et al.* 2003; Stockinger 1981). Hypokalemia is a key feature of barium toxicity (Koch *et al.* 2003). Depending on the dose and solubility of the barium salt, death may occur in a few hours or days (Stockinger 1981).

In 1994, NTP completed a subchronic study on barium using mice and rats (10 animals per dose group per sex). Male and female B6C3F1 mice received barium chloride dihydrate in drinking water at concentrations of 0, 125, 500, 1000, 2000 and 4000 mg/L for 13 weeks. Toxicologically significant effects (nephropathy and mortality) were reported in male and female mice at 4000 mg/L in drinking water. A drinking water concentration of 2000 mg/L (dose rates of 205 mg/kg bw/day in males and 200 mg/kg bw/day in females) was considered to represent the subchronic NOAEL (NTP 1994).

In the rat portion of the study, groups of male and female F344/N rats were exposed to barium chloride dihydrate in drinking water at concentrations of 0, 125, 500, 1000, 2000 and 4000 mg/L for 13 weeks. Toxicologically significant effects (increased kidney weights) were reported in female rats at water concentrations of 2000 mg/L (or a dose rate of 115 mg/kg bw/day: *i.e.*, the LOAEL) while the subchronic NOAEL was determined to be a drinking water concentration of 1000 mg/L (or a dose rate of 65 mg/kg bw/day for both sexes) (NTP 1994).

In an NTP chronic study (1994) male and female mice and rats were exposed to 0, 500, 1250 or 2500 mg/L barium chloride dihydrate in drinking water (mice: male=103 weeks; female=104 weeks; rats: male=104 weeks, female=105 weeks). Toxicologically significant effects (severe nephropathy and decreased survival) were reported in male and female mice at 2500 mg/L in drinking water (160 mg/kg bw/day in males and 200 mg/kg bw/day in females). A drinking water concentration of 1250 mg/L (dose rates of 75 mg/kg bw/day in males and 90 mg/kg bw/day in females) represented the chronic NOAEL in mice. In rats, the most sensitive toxicological effect was increased kidney weight. Female rats were the most sensitive group and a LOAEL of 2500 mg/L (75 mg/kg bw/day) was reported while the NOAEL was determined to be 1250 mg/L (45 mg/kg bw/day).

Barium is not likely to be carcinogenic to humans following oral exposure (US EPA 1998). There is no evidence of barium carcinogenicity in extremely limited lifetime bioassays of rats and mice exposed to 5 mg/L in drinking water, based solely on gross examination of tumours at autopsy (Schroeder and Mitchener, 1975a; b). In addition, the NTP (1994) found no evidence of carcinogenicity in chronic mice and rat studies. The US EPA (1998, 2004) stated that adequate chronic oral studies in rodents have not demonstrated carcinogenicity and it is not likely to be carcinogenic via this route. The inhalation route has not been adequately evaluated to classify barium in regard to carcinogenicity.

For evaluation of oral exposures the reference dose (RfD) of 0.2 mg/kg bw/day recommended by US EPA (2005) based on nephropathy observed in mice in the 1994 NTP study. Using benchmark dose modelling, a BMDL<sub>05</sub> of 63 mg/kg bw/day was selected as a point of departure for the RfD. Ten-fold uncertainty factors were applied for extrapolation for interspecies differences and intraspecies variation along with a 3-fold uncertainty factor to account for deficiencies in the database.

At the present time there is insufficient evidence to support a relative oral bioavailability for barium in soil of less than 100% for the purposes of guideline development.

Inhalation and dermal studies in humans and animals are not of sufficient quality to derive pathway specific TDIs for barium at the present time.

## **Guideline Derivation**

Canadian soil quality guidelines are derived for different land uses following the process outlined in CCME (2006) using different receptors and exposure scenarios for each land use. Detailed derivations for the soil quality guidelines for barium are provided in the scientific criteria document (CCME 2013).

## Soil Quality Guidelines for Environmental Health

Environmental soil quality guidelines  $(SQG_E)$  are primarily based on the soil contact pathway 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 protect foraging livestock and wildlife. To provide a broader scope of protection, a nutrient and energy cycling check is calculated for all land uses to protect critical microbial processes. For industrial land use, an off-site migration check is also calculated to prevent contamination of adjacent and more sensitive land uses.

The environmental soil quality guidelines for barium were not updated in 2012, and the conclusions of the 1999 barium *Soil Quality Guidelines for Environmental Health* remain in effect (CCME 1999):

"In the case of barium, there are insufficient data and/or confounding factors in the existing data to derive the preliminary soil contact values or the nutrient and energy cycling checks. Thus, the interim soil quality criteria (CCME 1991) are recommended as the  $SQG_{ES}$  for all land uses (Table 3)."

For more information on the environmental soil quality guidelines for barium, and its effects on ecological receptors, consult EC (1999).

### Soil Quality Guidelines for Human Health

For threshold contaminants, human health soil quality guidelines for direct contact (ingestion, inhalation and dermal contact) require a TDI for the most sensitive receptor for a given land use. In the absence of a Health Canada TDI for barium, the US EPA TDI of 0.2 mg/kg-d (US EPA 2005) was used in the derivation of the soil quality guidelines. Ingestion, inhalation and dermal contact guidelines were calculated for each of the four land uses specified by CCME (2006). The relative absorption factors for inhalation, ingestion are assumed to be 100%, by default. For dermal exposure the relative absorption factor is assumed to be 10% (Health Canada 2010).

CCME (2006) recommends a multimedia approach to guidelines development in which a default of 20% of the residual tolerable daily intake (*i.e.*, 20% x [TDI minus the Estimated Daily Intake or EDI]) is allocated to soil. Therefore, a soil allocation factor of 0.2 was applied in the derivation of the guideline.

Various check mechanisms are applied, if relevant, to the human health soil quality guidelines in order to provide them with a broader scope of protection, such as the potential to adversely impact groundwater, agricultural crops and livestock (Table 2).

A guideline for the protection of groundwater used as a source of raw water for drinking was not derived for barium due to constraints on the mathematical model when applied to inorganic compounds (CCME 2006).

An off-site migration check was carried out for commercial and industrial land uses only. Transfers of contaminated soil from one property to another are possible by environmental occurrences such as wind and water erosion (CCME 2006). The off-site migration check for commercial and for industrial land uses was determined to be 96 000 mg/kg (2 significant digits), which is more than the SQG<sub>HH</sub> for commercial (10 000 mg/kg) but less than the SQG<sub>HH</sub> for industrial (130 000 mg/kg) land uses. Therefore, only the industrial SQG<sub>HH</sub> needs to be modified to protect against off-site migration.

A check mechanism for produce, meat and milk was not carried out, since the produce, meat and milk check pertains to substances that are expected to bioconcentrate or biomagnify. It is noted that the  $SQG_{HH}$  are considered to be protective at most sites; however certain exposure pathways have not been evaluated in the development of the  $SQG_{HH}$ .

# Soil Quality Guidelines for Barium

The soil quality guidelines are intended to be protective of environmental health. Where sufficient and adequate data exist, the interim soil quality criteria (CCME 1991) are superseded.

There are sufficient data to derive the  $SQG_{HH}$ . However, there are insufficient or inadequate data (as of 1999) to derive the  $SQG_E$ . For barium the interim soil quality criteria (CCME 1991) are lower than the  $SQG_{HH}$  derived in this report. Therefore, the interim soil quality criteria have been retained as the SQG for barium for all land uses.

	Land use				
	Agricultural	Residential/ parkland	Commercial	Industrial	
Guideline	<b>750</b> <sup>a</sup>	<b>500</b> <sup>a</sup>	<b>2000</b> <sup>a</sup>	<b>2000</b> <sup>a</sup>	
Human health guidelines/check values					
SQG <sub>HH</sub>	6800 <sup>b</sup>	6800 <sup>b</sup>	10 000 <sup>b</sup>	96 000 <sup>b</sup>	
Direct contact guideline	6800 <sup>c</sup>	6800 <sup>c</sup>	10 000 <sup>c</sup>	130 000 <sup>c</sup>	
Inhalation of indoor air check	NC <sup>d</sup>	NC <sup>d</sup>	NC <sup>d</sup>	NC <sup>d</sup>	
Off-site migration check	_	_	96 000	96 000	
Groundwater check (drinking water)	NC <sup>e</sup>	NC <sup>e</sup>	NC <sup>e</sup>	NC <sup>e</sup>	
Produce, meat, and milk check	NC <sup>f</sup>	NC <sup>f</sup>			
Environmental health guidelines/check values					
SQG <sub>E</sub>	NC <sup>g</sup>	NC <sup>g</sup>	NC <sup>g</sup>	NC <sup>g</sup>	
Soil contact guideline	NC	NC	NC	NC	
Soil and food ingestion guideline	NC	_	_		
Nutrient and energy cycling check	NC	NC	NC	NC	
Off-site migration check	_	_	NC	NC	
Groundwater check (aquatic life)	NC <sup>e</sup>	NC <sup>e</sup>	NC <sup>e</sup>	NC <sup>e</sup>	
1999 Barium Soil Quality Guideline (CCME 1999)	750	500	2000	2000	
Interim soil quality criterion (CCME 1991)	750	500	2000	2000	

Table 2. Soil quality guidelines and check values for barium (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 only a SQG<sub>HH</sub>. It is greater than the corresponding interim soil quality criteria (CCME 1991). Therefore the interim soil quality criterion (and 1999 soil quality guideline) is retained as the soil quality guideline for this land use.

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

<sup>c</sup>The direct human health-based soil quality guideline is based on direct exposure to soil ingestion, dermal contact, and particulate inhalation.

<sup>d</sup>The inhalation of indoor air check applies to volatile organic compounds and is not calculated for metal contaminants.

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

<sup>f</sup>This check is intended to protect against chemicals that may biomagnify in human food. Barium is not expected to exhibit this behaviour, therefore this pathway was not evaluated.

<sup>g</sup>Data are insufficient/inadequate to calculate an  $SQG_E$ , or provisional  $SQG_E$  for this land use. The environmental soil quality guidelines for barium were not updated in 2012. For more information on the environmental soil quality guidelines for barium and its effects on ecological receptors, consult EC (1999).

#### References

- Adriano, D.C. 1986. Barium. Trace Elements in the Terrestrial Environment. Springer-Verlag, New York, Berlin, Heidelberg, Tokyo. pp. 494-496.
- AENV (Alberta Environment), 2004. Soil Quality Guidelines for Barite: Environmental Health and Human Health. Science and Standards Branch, Alberta Environment. ISBN No. 0-7785-3164-3. Available at

http://www.environment.gov.ab.ca/info/library/6298.pdf

- Alberta Health. 1998. Assessing Air Quality in High Level Report 1: A Preliminary Analysis of Physician Visits and Air Particulate Data. Prepared for Northwestern Health Services Region # 17.
- ATSDR (Agency for Toxic Substances and Disease Registry). 1992. Public Health Assessment Guidance Manual. U.S. Department of Health and Human Services. PB92-147164.
- ATSDR (Agency for Toxic Substances and Disease Registry). 2007. Toxicological Profile for Barium and Barium Compounds. U.S. Department of Health and Human Services: http://www.atsdr.cdc.gov/toxprofiles/tp24.html
- Boffito, C. 1991. Barium. In: Kirk-Othmer Encyclopedia of Chemical Technology. 4th edition, vol. 3. John Wiley and Sons, New York, Chichester, Brisbane, Toronto and Singapore. pp. 902-908.
- Borzelleca, J.F., L.W. Condie Jr., and J.L. Egle Jr. 1988. Short term toxicity (one-and ten day average) of barium chloride in male and female rats. J. Amer. College Tox. 7(5): 675-685.

Buchanan, R.J. 1985. Personal communication. Water Management Branch, B.C. Ministry of Environment. In: CCREM, 1987.

- CCME (Canadian Council of Ministers of the Environment). 1991. Interim Canadian Environmental Quality Criteria for Contaminated Sites - The National Contaminated Sites Remediation Program. Report CCME EPC-CS34, September 1991.
- CCME. 1999. Canadian soil quality guidelines for the protection of environmental and human health: Barium (1999). In. Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environment, Winnipeg.
- CCME. 2006. Protocol for the Derivation of Soil Quality Guidelines. PN 1332. Winnipeg, Manitoba. Available at:
- http://www.ccme.ca/assets/pdf/sg\_protocol\_1332\_e.pdf. CCME 2013. Canadian Soil Quality Guidelines for Barium: Protection of Human Health. Scientific Criteria Document. Winnipeg.
- CCREM (Canadian Council of Resource and Environmental Ministers). 1987. Canadian Water Quality Guidelines. Prepared by the Task Force on Water Quality Guidelines of the Canadian Council of Resource and Environment Ministers. March 1987.
- Chaudry, F.M.A., A. Wallace and Mueller, R.T. 1977. Commun. Soil Sci. Plant Anal. 8: 795-797. In: Adriano, 1986.
- Cherry, D.S. and R.K. Guthrie. 1979. The uptake of chemical elements from coal ash and settling basin effluent by primary producers II. Relation between concentrations in ash deposits and tissues of grasses growing on the ash. Sci. Total Environ. 13: 27.
- CICAD (Concise International Chemical Assessment Document) 33. 2001. Barium and Barium Compounds. United Nations Environment Programme, International Labour Organization, and World Health Organization. Geneva. Available at:
- http://www.inchem.org/documents/cicads/cicads/cicad33.htm.
- Dabeka, R.W., X.-L. Cao and J. Moisey. 2010. Dietary intakes of trace elements for the years 2003 - 2007 (unpublished data). Obtained from the Food Research Division, Bureau of Chemical Safety, Health Products and Food Branch.
- Davis, W.E. 1972. National Inventory of Sources and Emissions: Barium, Boron, Copper, Selenium and Zinc. U.S. Environmental Protection Agency, Washington., D.C. Report EPA-68-02-0100. P.56. In: WHO, 1990 and ATSDR, 1992.
- DiBello, P.M., J.L. Manganaro, and E.R. Aguinaldo. 1991. Barium compounds. In: Kirk-Othmer Encyclopedia of Chemical Technology. 4th edition, vol. 3. John Wiley and Sons, New York, Chichester, Brisbane, Toronto and Singapore. pp. 909-931.

Dumont 2007. Barite and Witherite. Canadian Minerals Yearbook.

- EC (Environment Canada). 1996. The State of Canada's Environment -1996, Environment Canada, Ottawa, Ontario. SBN 0-660-16368-3.
- EC (Environment Canada). 1999. Canadian Soil Quality Guidelines for Barium: Environmental Effects. Scientific Supporting Document. National Guidelines and Standards Office, Environment Canada, Ottawa.
- EC (Environment Canada). 2011. The National Air Pollution Surveillance Network. Available at: <u>http://www.etc-</u> <u>cte.ec.gc.ca/NapsAnnualRawData</u>. For password contact Claire Austin at Claire.Austin@ec.gc.ca.
- Grace, J.K. 1990. Oral toxicity of barium metaborate to the Eastern subterranean termite (Isoptera:Rhinotermitidae). J. Entmol. Sci. 25(1): 112-116.
- Grace, J.K. and A. Abdallay. 1990. Termiticidal activity of boron dusts (Isoptera, Rhinotermitidae). J. Appl. Ent. 109: 282-288.
- Graney, J.R., M.S. Landis and G.A. Norris. 2004. Concentrations and solubility of metals from indoor and personal exposure PM2.5 samples. Atmospheric Environment 38: 237–247
- Grunsky, E.C. 2010. Geochemical Background in Soil and Till from Selected Areas across Canada, including New Brunswick and the Maritime Provinces Soil Survey. Geological Society of Canada, Natural Resources Canada. 2010.

- Gizyn, W. I. 2002. Phytotoxicology 1999, 2000 and 2001 Investigations: Safety-Kleen Limited - Moore Township. Toronto, Ontario, Ontario Ministry of the Environment, Standards Development Branch, Ecological Standards and Toxicology Section.
- Health Canada. 2010. Preliminary Federal Contaminated Site Risk Assessment in Canada, Part II: Guidance on Human Health Preliminary Quantitative Risk Assessment (PQRA), Version 2.0. Contaminated Sites Division, Safe Environments Directorate, Health Canada, Ottawa.
- Health Canada. 2011. Draft Estimated Daily Intake Development Methodology – Barium. Contaminated Sites Division. Safe Environments Directorate, Health Canada, Ottawa.
- Hildebrand, S.G., R.M. Cushman and J.A. Carter, 1976. The potential toxicity and bioaccumulation in aquatic systems of trace elements present in aqueous coal conversion effluents. In: Trace Substances in Environmental Health, D.D. Hemphill (Ed.). University of Missouri, Columbia, Missouri.
- HSDB (Hazardous Substances Database). 2003. Barium Compounds. Available at: <u>http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB</u>. 2004.
- Johnson, D., A.L. Mehring, and H.W. Titus. 1960. Tolerance of chickens for barium. PSEBM (Proceedings of the Society for Experimental Biology and Medicine) 104:436–438.
- Jourdan S, M. Bertoni, P. Sergio, P. Michele and M. Rossi. 2001. Suicidal poisoning with barium chloride. Forensic Sci Int 119(2): 263-265.
- Koch M, O. Appoloni, V. Haufroid, J.L. Vincent and P. L'Heureux. 2003. Acute barium intoxication and hemodiafiltration. J Toxicol Clin Toxicol 41(4):363-367.
- Miner, S. 1969. Preliminary air pollution survey of barium and its compounds. A literature review. Prepared under Contract No. PH 22-68-25 USDHEW, Public Health Service, National Air Pollution Control Administration, Raleigh, NC.
- NAS (National Academy of Sciences). 1977. Drinking water and health. Vol. 1. National Research Council, Washington, DC.
- Nelson, D.W., S.L. Liu and L.E. Sommers. 1984. Extractability and plant uptake of trace elements from drilling fluids. J. Environ. Qual. 13: 562..
- NRCan. 2003. Mining and Mineral Processing Operations in Canada, Natural Resources Canada. Available at: <u>http://mmsd1.mms.nrcan.gc.ca/mmsd/producers/bycommodity\_result\_e.asp?material=Barite&category=N. 2004.</u>
- NTP (National Toxicology Program). 1994. NTP Technical Report on the Toxicology and Carcinogenesis Studies of Barium Chloride Dihydrate in F344/N Rats and B6C3F1 Mice (Drinking Water Studies). National Toxicology Program, Public Health Service, US Department of Health and Human Services, Research Triangle Park, NC. NIH Pub PB94-214178. Cited in: US EPA, 2004.
- Rai, D., J.M.Zachara, A.P. Schwab, R.A. SchmidtD.C Girvin and J.E. Rogers. 1984. Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration. Vol. 1: A Critical Review. Prepared by Pacific Northwest Laboratories, Richland, Washington. Report EA-3356. Electric Power Research Institute, Palo Alto, CA. In: ATSDR, 1992.
- Rasmussen, P. E., K. S. Subramanian and B. J. Jessiman. 2001. A multielement profile of house dust in relation to exterior dust and soils in the city of Ottawa, Canada. Science of the Total Environment 267(1-3): 125-140.
- Reeves, A.L. 1986. Barium. In: Handbook on the Toxicology of Metals -Vol. II: Specific Metals, L. Friberg, G.F. Nordberg and B. Velimir (Eds). Elsevier Science Publishers, Amsterdam, Oxford, New York. pp.84-93.
- Robinson, W.O., R.R. Whetstone and G. Edgington. 1950. The occurrence of barium in soils and plants. U.S. Dept. Agric. Tech. Bull. 1013: 1-36. In: WHO, 1990.

#### BARIUM

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

- Schroeder, H.A. and M. Mitchener. 1975a. Life-term studies in rats: Effects of aluminum, barium, beryllium and tungsten. J. Nutr. 105: 421.
- Schroeder, H.A. and M.Mitchener. 1975b. Life-term effects of mercury, methyl mercury and nine other trace elements on mice. J. Nutr. 105: 452.
- Schroeder, H.A. 1970. Barium. American Petroleum Institute, Washington D.C. Air Monograph No. 70-12. In: WHO, 1990 and ATSDR, 1992.
- Stockinger, H.E. 1981. The metals. In: Patty's industrial hygiene and toxicology. Vol. II(A). G.D. Clayton and F.E. Clayton (eds.). J. Wiley, New York, NY. p. 1531.
- Taylor, D.M., P.H. Bligh and M.H. Duggan. 1962. The absorption of calcium, strontium, barium and radium from the gastrointestinal tract of the rat. Biochem. J. 83: 25.
- US EPA (United States Environmental Protection Agency). 1998. Toxicological Review of Barium and Compounds. US Environmental Protection Agency, Washington, DC. March 1998 (with minor revisions January 1999).

- US EPA (United States Environmental Protection Agency). 2004. Integrated Risk Information System (IRIS) (on-line database). US Environmental Protection Agency, Washington, DC.
- US EPA (United States Environmental Protection Agency). 2005. Toxicological Review of Barium and Compounds. U.S. Environmental Protection Agency, Washington, DC. June 2005 (reference does revised). Available at: http://www.epa.gov/iris/toxreviews/0010-tr.pdf.

US EPA (United States Environmental Protection Agency). 2009. Human Exposure Database System (HEDS) Available at: <u>http:</u> oaspub.epa.gov/heds/study\_list\_frame.

- Venugopal, B. and T.D. Luckey. 1978. Metal Toxicity in Mammals: Chemical Toxicity of Metals and Metalloids. Plenum Press, New York. In: WHO, 1990.
- WHO (World Health Organization). 1990. Environmental Health Criteria 107: Barium. International Programme on Chemical Safety, Geneva. 121 pp.

#### **Reference listing:**

Canadian Council of Ministers of the Environment. 2013. Canadian soil quality guidelines for the protection of environmental and human health: Barium. In: Canadian environmental quality guidelines, Canadian Council of Ministers of the Environment, Winnipeg.

For further scientific information, contact:

Environment Canada National Guidelines and Standards Office 200 Sacré-Cœur Blvd. Gatineau, QC K1A 0H3 Phone: (819) 953-1550 E-mail: ceqg-rcqe@ec.gc.ca http://www.ec.gc.ca/ceqg-rcqe For additional copies, contact:

www.ccme.ca

Aussi disponible en français.

© Canadian Council of Ministers of the Environment 2013 Excerpt from Publication No. 1299 ISBN 1-896997-34-1