Draft Screening Assessment

Thallium and its compounds

Environment and Climate Change Canada
Health Canada

September 2020

Synopsis

Pursuant to section 68 and 74 of the *Canadian Environmental Protection Act, 1999* (CEPA), the Minister of the Environment and the Minister of Health have conducted a screening assessment of thallium and its compounds. The scope of this assessment is on the thallium moiety. This assessment considers all thallium-containing substances, that may release thallium as well as thallium in its elemental form, and thallium released in the environment in dissolved, solid or particulate forms. This includes three thallium-containing substances on the *Domestic Substances List* (DSL) identified as priorities for assessment as they met categorization criteria under subsection 73(1) of CEPA or were considered a priority on the basis of other ecological concerns, and two thallium-containing substances that were identified for further consideration following prioritization of the Revised In Commerce List (R-ICL).

The Chemical Abstracts Service Registry Numbers (CAS RN[1]), their DSL or R-ICL names and their common names are listed in the table below.

Thallium-containing substances identified as priorities for assessment

CAS RN	DSL or R-ICL name	Common name
7440-28-0 [a]	Thallium	Thallium
563-68-8	Acetic acid, thallium(1++) salt	Thallium(I) acetate
7791-12-0	Thallium chloride	Thallium chloride
10031-59-1 [b]	Sulfuric acid, thallium(1+) salt (1:?)	Thallium(I) sulfate
55172-29-7 [b]	Thallium chloride (^{201}TlCl)	^{201}TlCl

[a] This substance was not identified under subsection 73(1) of CEPA but was included in this assessment as it is highly reactive when exposed to moisture in air and releases thallium ions under environmental conditions.

[b] This substance was not identified under subsection 73(1) of CEPA but was included in this assessment as it was identified for further consideration following prioritization of the Revised In Commerce List (R-ICL).

Thallium exists in the earth's crust at an average concentration of 0.7 mg/kg. It is typically associated with sulfide ores of various metals including zinc, copper, iron, and lead, and is also present in coal. Thallium is present in many natural minerals as well as in meteorites, volcanic rocks, plants, and trace amounts in most living organisms.

Anthropogenic sources of thallium are primarily associated with the incidental production and releases of residues/by-products from various industrial activities, such as smelting/refining processes, metal mining, and fly ashes of coal-fired electrical power plants. Thallium production is low with less than 9 tonnes produced globally in 2017.

Three thallium substances (CAS RN 563-68-8, 7791-12-0 and 10031-59-1) were included in a survey issued pursuant to a CEPA section 71 notice. In 2011, 100 – 1000

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kg/yr of thallium chloride (CAS RN 7791-12-0) was manufactured in Canada. There were no other reports of manufacture or imports above the reporting threshold of 100 kg/yr. Less than 30 kg of thallium were imported into Canada in 2017.

The main uses of thallium substances include use in semiconductors and the laser industry, fiber (optical) glasses, photoelectric cells, and high temperature superconductors, as activators in gamma radiation detection equipment (scintillometer), and as intermediates in chemical production. Other uses include use in low temperature thermometers, mercury arc lamps, alloys with other metals, jewellery, fireworks, pigments and dyes, and for mineralogical separation. Additional uses of thallium in Canada are in products available to consumers: as a radiopharmaceutical in human drug products and as a medicinal ingredient in homeopathic licensed natural health products. Thallium may also be used as a component in food packaging materials.

Thallium exists in two oxidation states in the aquatic environment: monovalent thallous Tl(I) (i.e., Tl^+) and trivalent thallic Tl(III) (i.e., Tl^{3+}). The highly soluble and weakly reactive Tl(I) ion is the more bioavailable thallium species in both aquatic and terrestrial environments. The precipitation of inert $Tl(OH)_3$ may be an effective mechanism for removing thallium from water. However, thallium may be remobilized from sediments and enter the water column under anoxic conditions where Tl(III) will be reduced to Tl(I). Therefore, Tl(I) is the focus of this screening assessment.

Thallium is considered to be persistent (as are all elements). Thallium is not an essential element for organisms. Organisms exposed to thallium in their habitats readily take up thallium by either direct contact with environmental media (dermal or respiratory exposure) or by ingesting food through the gastrointestinal tract. Elevated thallium concentrations have been observed in organisms living near sources of releases (e.g., smelters). Thallium may be considered bioaccumulative in aquatic and soil-dwelling organisms and plants. The potential for thallium to biomagnify in both aquatic and terrestrial food chains is uncertain due to very limited and contradictory data presently available.

Thallium causes mortality as well as growth and reproductive effects to both aquatic and terrestrial organisms at very low concentrations. The chronic predicted no-effect concentrations (PNECs) for thallium for aquatic organisms were derived from reliable ecotoxicity studies. Current information available for thallium soil toxicity indicate that a PNEC identical to the 1999 CCME (Canadian Council of Ministers of the Environment) guideline is protective of soil-dwelling organisms and plants in the Canadian environment.

Risk quotient (RQ) analyses were performed by comparing predicted environmental concentrations with PNECs to determine the potential for ecological harm in Canada. Of the facilities examined, one facility in the metal mining sector showed ecological risk from effluent releases of Tl, two stand-alone facilities in the base metals sector showed potential ecological risk, and one facility in the coal-powered energy sector showed potential for ecological risk due to releases of Tl from its lagoon effluents. This analysis

indicates that there is a potential for thallium to cause ecological harm in the aquatic environment as a result of its release from multiple sectors at sites located across Canada.

Considering all available lines of evidence presented in this draft screening assessment, there is risk of harm to the environment from thallium and its compounds. It is proposed to conclude that thallium and its compounds meet the criteria under paragraph 64(*a*) of CEPA as they are entering or may enter the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. However, it is proposed to conclude that thallium and its compounds do not meet the criteria under paragraph 64(*b*) of CEPA as they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger to the environment on which life depends.

Thallium and its compounds were evaluated using the Biomonitoring-based Approach 2 which compares human biomonitoring data (exposure) against biomonitoring guidance values (health effects), such as human biomonitoring values (HBM-I) to identify substances with low concern for human health. Thallium concentrations were measured in urine of North Americans as part of the Canadian Health Measures Survey and the National Health and Nutrition Examination Survey (NHANES) in the United States. A human biomonitoring guidance value (HBM-I) established by the German Federal Environmental Agency is considered to be protective of adverse health effects of thallium in humans. Median and 95th percentile urinary thallium concentrations in Canadians of 0.21 and 0.55 µg/g creatinine were lower than the HBM-I value of 6.4 µg/g creatinine. Therefore, thallium and its compounds are considered to be of low concern to human health at current levels of exposure.

On the basis of the information presented in this draft screening assessment, it is proposed to conclude that thallium and its compounds do not meet the criteria under paragraph 64(*c*) of CEPA, as they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health.

Therefore, it is proposed to conclude that thallium and its compounds meet one or more of the criteria set out in section 64 of CEPA.

It is also proposed that thallium and its compounds meet the persistence criteria as set out in the *Persistence and Bioaccumulation Regulations* of CEPA. It is considered that thallium and its compounds are easily assimilated by various organisms and have the potential to accumulate in both aquatic and terrestrial organisms. However, no conclusion can be reached on the potential of thallium biomagnification in both aquatic and terrestrial food chains considering the limited and contradictory data currently available.

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List of Tables and Figures

1. Introduction

Pursuant to section 68 and 74 of the *Canadian Environmental Protection Act, 1999* (CEPA) (Canada 1999), the Minister of the Environment and of the Minister of Health have conducted a draft screening assessment of thallium and its compounds to determine whether these substances present or may present a risk to the environment or to human health. Five thallium-containing substances (listed in Table 2-1) were identified as priorities for assessment as they met categorization criteria under subsection 73(1) of CEPA, were considered a priority on the basis of other ecological concerns (ECCC, HC, modified 2017), or were identified for further consideration following prioritization of the Revised In Commerce List (R-ICL)[2] (ECCC, HC [modified 2017], Health Canada [modified 2017]).

This draft screening assessment focuses on the thallium moiety, and thereby considers thallium in its elemental form, thallium-containing substances and thallium released in dissolved, solid or particulate form. It does not address counter-ions present in thallium-containing substances (e.g., oxide, chloride). Unless otherwise indicated, throughout this report the term "thallium" refers to both elemental thallium and its compounds. As such, it is not limited to consideration of the five substances identified as priorities for assessment. All substances that have the potential to dissolve, dissociate and/or degrade to release thallium through various transformation pathways can potentially contribute to the exposure of humans and other living organisms to bioavailable forms of thallium. This assessment considers combined exposure to the thallium moiety, whether it is present in environmental media (e.g., water, sediment, soil, air), as well as food or products that may result from natural or anthropogenic sources.

In the environment, thallium compounds may be released naturally from weathering or breakdown of soils or rocks, and through forest fires. Incidental production and release of thallium-containing substances as residues/by-products in industrial processes is the primary anthropogenic source of thallium release into the environment. Environmental monitoring data is the primary line of evidence used to develop the ecological exposure characterisation of certain sectors or activities that have the potential to release thallium to the environment. The interpretation of thallium monitoring data considered measurements of total concentrations of thallium in environmental media, food, products, and humans. Where feasible, background or reference concentrations were differentiated from concentrations attributed to anthropogenic sources.

This draft screening assessment includes consideration of information on physical-chemical properties, environmental fate, hazards, uses, releases, and exposures. Relevant data were identified up to July 2018. Empirical data from key studies were critically reviewed and used to reach proposed conclusions. When available and

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[2] The Revised In Commerce List (R-ICL) is a list of substances that are known to have been authorized for use in commerce in Canada between 1987 and 2001. As the substances are present in Canada, the government is addressing them for potential impact on human health and the environment, in order to risk-manage the substances if required.

relevant, information presented in assessments from other jurisdictions was also considered.

This draft screening assessment was prepared by staff in the CEPA Risk Assessment Program at Health Canada and Environment and Climate Change Canada and incorporates input from other programs within these departments. The ecological portion of this assessment has undergone external review and/or consultation. Comments on the technical portions relevant to the environment were received from Dr. Carrie Rickwood (Natural Resources Canada), Dr. Claude Fortin (Institut national de la recherche scientifique, INRS), and Geoff Granville (GCGranville Consulting Corp). The human health portion of this assessment is based on the Biomonitoring-based Approach 2 Science Approach Document (SciAD) (published December 9, 2016), which was externally peer-reviewed and subject to a 60-day public comment period. External peer-review comments were received from Lynne Haber and Andrew Maier from Toxicology Excellence for Risk Assessment (TERA) and Judy LaKind from LaKind Associates. While external comments were taken into consideration, the final content and outcome of the screening assessment remain the responsibility of Health Canada and Environment and Climate Change Canada.

This draft screening assessment focuses on information critical to determining whether substances meet the criteria as set out in section 64 of CEPA by examining scientific information and incorporating a weight of evidence approach and precaution.[3] This draft screening assessment presents the critical information and considerations on which the proposed conclusion is based.

2. Identity of substances

Thallium is a naturally occurring element belonging to group 13 of the periodic table. Thallium exists primarily in two valence states: monovalent (thallous), Tl(I), and trivalent (thallic), Tl(III). The oxidation potential for the reaction Tl(I) to Tl(III) is very low (-1.28 V), and Tl(I) halides have a much higher lattice energy compared to Tl(III) halides (Lin and Nriagu 2011).

The focus of this assessment is on the thallium moiety. This assessment considers all thallium-containing substances that may release thallium as well as thallium in its

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[3]A determination of whether one or more of the criteria of section 64 of CEPA are met is based upon an assessment of potential risks to the environment and/or to human health associated with exposures in the general environment. For humans, this includes, but is not limited to, exposures from ambient and indoor air, drinking water, foodstuffs, and products available to consumers. A conclusion under CEPA is not relevant to, nor does it preclude, an assessment against the hazard criteria specified in the *Hazardous Products Regulations*, which are part of the regulatory framework for the Workplace Hazardous Materials Information System for products intended for workplace use. Similarly, a conclusion based on the criteria contained in section 64 of CEPA does not preclude actions being taken under other sections of CEPA or other acts.

elemental form, and thallium released in the environment in dissolved, solid or particulate forms, including five thallium-containing substances listed on the *Domestic Substances List* (DSL) or the Revised In Commerce List (R-ICL).

The Chemical Abstracts Service Registry Numbers (CAS RN[4]), DSL and R-ICL names and common names for the five remaining priorities for assessment in the draft screening assessment of thallium and its compounds are presented in Table 2-1.

Table 2-1. Substances identified as priorities for assessment

CAS RN	DSL or R-ICL name (common name)	Molecular formula	Molecular weight (g/mol)
7440-28-0 [a]	Thallium	Tl	204.38
563-68-8	Acetic acid, thallium(1++) salt (Thallium(I) acetate)	$Tl\text{-}C_2H_3O_2$	263.43
7791-12-0	Thallium chloride (Thallium(I) chloride)	TlCl	239.84
10031-59-1[b]	Sulfuric acid, thallium (1+) salt (1:?) (Thallium sulfate)	Tl_2SO_4	504.83
55172-29-7 [b,c]	Thallium chloride (^{201}TlCl)	^{201}TlCl	236.42

[a] This substance was not identified under subsection 73(1) of CEPA but was included in this assessment as it is highly reactive when exposed to moisture in air and will release bioavailable thallium ion under environmental conditions.

[b] This substance was not identified under subsection 73(1) of CEPA but was included in this assessment as it was identified for further consideration following prioritization of the Revised In Commerce List (R-ICL).

[c] Radioactive.

3. Physical and chemical properties

Thallium metal is insoluble in water but is highly reactive. The surface of the metal oxidizes to form a coating of thallium oxide when exposed to air and moisture, then forms thallium hydroxide in water with a solubility of 259 g/L (ATSDR 1992; Frattini 2005). Thallium forms alloys with other metals and easily amalgamates with mercury. It also reacts with numerous compounds to form stable salts (ATSDR 1992; CCME 1999; Frattini 2005; IPCS 1996).

The ionic radii and the electronegativity constant of thallous are similar to those of alkali metals (e.g., potassium); whereas thallic compounds are less basic, resembling aluminium (Frattini 2005). The water solubility of thallous salts generally range from

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soluble to very soluble (Table 3-1), except for the sulfide (Tl_2S, pK_{sp} = 20) (Lide 2005). The solubility of Tl(III) compounds (e.g., $Tl(OH)_3$, pK_{sp} = 45.2) in water is generally low and dependent on pH; soluble Tl(III) ions can exist only under extremely acidic conditions (Lin and Nriagu 1998).

A summary of physical and chemical property data (ATSDR 1992; IPCS 1996; Lide 2005) of thallium-containing substances identified as remaining priorities for assessment are presented in Table 3-1.

Table 3-1. Experimental physical and chemical property values (at standard temperature unless otherwise specified) for certain thallium compounds

Property	Thallium	Thallium(I) acetate	Thallium chloride	Thallium sulfate
Color	Bluish white	White	Colorless	White
Physical state	Solid	Solid	Solid	Solid
Melting point (°C)	304	131	430	632
Boiling point (°C)	1473	No data	720	Decomposes
Density at 20 °C (g/cm^3)	11.85	3.68	7.00	6.77
Water solubility at 20 °C (g/L)	Insoluble	Very soluble	0.33	48.7
Other solubilities	Soluble in nitric or sulfuric acid	Very soluble in alcohol; insoluble in acetone	Soluble in alcohol and ether	Soluble in diluted nitric acid and alcohol
Vapour pressure at 1000 °C (Pa)	1333	No data	No data	No data

4. Sources and uses

4.1 Natural sources

The average thallium content in the earth's crust is estimated to be approximately 0.7 mg/kg (USGS 2018). It is typically associated with sulfide ores of various metals including zinc, copper, iron, lead, and in coal (HSDB 1983-; IPCS 1996; Kazantzis 2000). Organic-rich shales and coals from the Jurassic period have been shown to contain thallium of up to 1000 mg/kg (Kazantzis 2000). It is also present in many minerals (e.g., along with potassium, cesium, and rubidium) in trace amounts. Certain natural minerals such as crookesite (($Cu,Tl,Ag)_2Se$), lorandite ($TlAsS_2$), hutchinsonite (($Tl,Pb)_2As_5S_9$), and avicennite (Tl_2O_3) contain up to 60% thallium (Reimann and Caritat

1998), but these minerals are rare (CCME 1999; HSDB 1983-; IPCS 1996). Thallium has also been detected in meteorites, volcanic rocks, plants, and in trace amounts in most living organisms.

4.2 Anthropogenic sources

Thallium is released from various industrial activities, such as residues of smelting/refining process, from sulphuric acid plants, from residue sulfide ores of lead, zinc, copper and iron, and from minerals associated with cadmium, iron, and potassium such as feldspars and micas (CCME 1999; USGS 2018). World reserves of thallium contained in zinc resources are estimated to be in the order of 17 million kilograms; they are mostly located in Canada, Europe, and the United States. World reserves in coal resources are estimated at 630 million kilograms (USGS 2018).

In 2017, global thallium production was less than 9 tonnes (USGS 2018).

Three thallium-containing substances (CAS RN 563-68-8, 7791-12-0, and 10031-59-1) have been included in surveys issued pursuant to a CEPA section 71 notice (Canada 2012, 2017a). In 2011, 100 – 1000 kg of thallium chloride (CAS RN 7791-12-0) was manufactured in Canada (Environment Canada 2013b). There were no other reports of manufacture or imports above the reporting threshold of 100 kg/yr for these three substances[5]. In addition, it was reported that less than 30 kg of thallium as unwrought, powders, and articles thereof were imported into Canada in the year 2017 (CIMT 2018).

4.3 Uses

The main uses of thallium substances include use in fiber (optical) glasses, photoelectric cells, as an activator in gamma radiation detection devices (scintillometers), in the semiconductor and laser industry (including use in high-temperature superconductors), and as intermediates in chemical production (ATSDR 1992; Peter and Viraraghavan 2005). Other uses include use in low-temperature thermometers, mercury arc lamps, alloys with other metals, jewellery, fireworks, pigments and dyes, for mineralogical separation, impregnation of wood and leather against fungi and bacteria (ATSDR 1992; CCME 1999; Peter and Viraraghavan 2005; USGS 2018). In addition, the radioactive isotope thallium-201 is used in imaging of the heart to determine the location and extent of coronary artery blockages, and scar tissue from previous heart attacks (Blumenthal et al. 2013). Thallium salts were also used in the past as a depilatory agent, to treat various diseases such as fungal infections, syphilis, tuberculosis, and gonorrhea, and as pesticides (bactericides, rodenticides, and insecticides). These historical uses have, however, been banned in most countries due to thallium's high toxicity, accumulation in the human body and persistence in the

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[5] Values reflect quantities reported in response to the survey conducted under section 71 of CEPA (Environment Canada 2013b). See survey for specific inclusions and exclusions (schedules 2 and 3).

environment (Peter and Viraraghavan 2005). In Canada, thallium sulfate based insecticides for ants were the only registered agricultural use, and they were completely discontinued in 1974 (Lang 1993, Agriculture Canada, Ottawa, pers. com. unreferenced, cited in CCME 1999). Additional uses of thallium in Canada are listed in Table 4-1.

Table 4-1. Additional uses of thallium in Canada

Use	Thallium
Food packaging materials [a]	Y
Medicinal ingredient in radiopharmaceuticals[b]	Y
Medicinal or non-medicinal ingredients in licensed natural health products [c]	Y

Abbreviations: Y = use was reported for this substance
[a] personal communication, emails from the Food Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated March 14, 2016; unreferenced, Health Canada 2016.
[b] Health Canada, 2016; DPD [modified 2018].
[c] Thallium is listed as a homeopathic substance in the Natural Health Products Ingredient Database. Homeopathic uses are regulated under the *Natural Health Products Regulations* (Canada 2003). Health Canada 2016; LNHPD [modified 2018]; NHPID [modified 2019].

5. Releases to the environment

Natural releases of thallium to the aquatic environment occur primarily by the weathering of minerals and rocks that contain thallium (CCME 1999). Soil erosion, forest fires, and volcanic activity can also contribute to thallium entering the aquatic environment naturally (Couture et al. 2011).

Since 2014, Canadian facilities must annually report releases, disposals and transfers for recycling of thallium (and its compounds) to the National Pollutant Release Inventory (NPRI) if they meet specific requirements (ECCC 2016), namely, if for a given calendar year over 100 kg of thallium was:
- Manufactured, processed or otherwise used at a concentration above 1%;
- Incidentally manufactured, processed or otherwise used as a by-product at any concentration;
- Contained in tailings at any concentration; and
- Contained in waste rock that is not inert and that is disposed of, at any concentration.

Figure 5-1 indicates the number of facilities in Canada that reported to the NPRI total environmental releases of thallium between 2014 and 2017 (NPRI 2018). During this period, the number of facilities reporting thallium increased from 19 to 42 and total yearly releases of thallium and its compounds to the environment via air, water, and land are in the range of 1 963 to 3 569 kg/year.
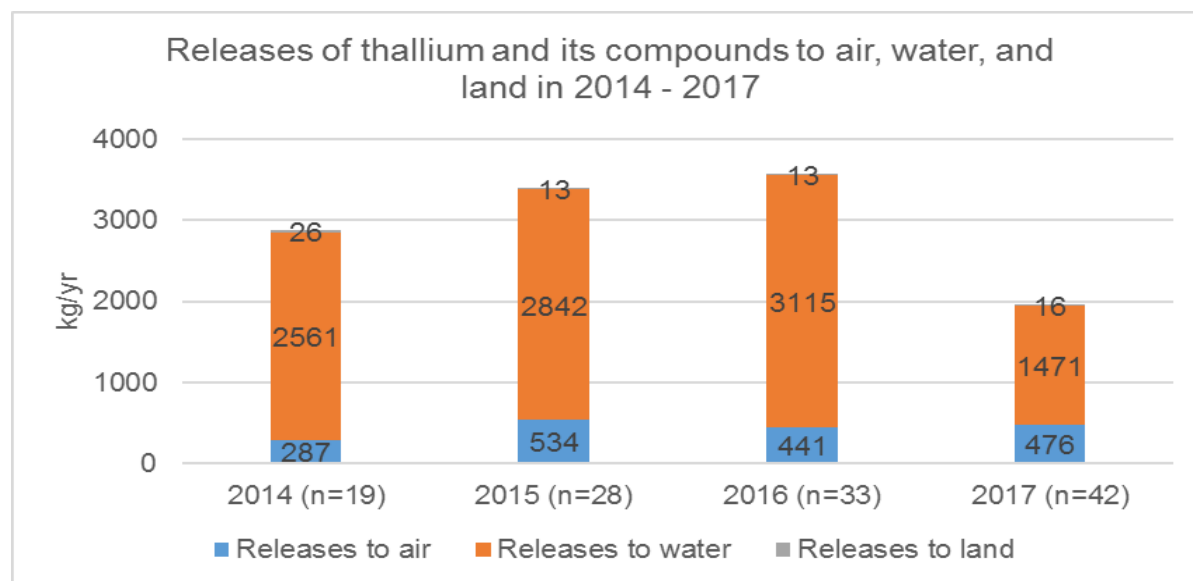
Figure 5-1. NPRI data on releases of thallium and its compounds (kg/year) to water, air, and land in 2014 – 2017

Figure 5-2 and 5-3 depict the total yearly releases to the environment via air and water by industrial sectors including: coal-fired power generating plants (electric power generation, transmission and distribution), metal ore mining, base metals smelters (non-ferrous metal (except aluminum) production and processing), and wastewater treatment plants (water, sewage and other systems) in 2014 to 2017. The land releases of thallium and its compounds are not shown by sectors due to small quantities by each sector. During this period, no facilities from the wastewater treatment sector reported thallium releases to air over the reporting threshold of 100 kg/year. Base metals smelters reported the highest thallium releases to air and water compared to other industrial sectors. Electric power generation, transmission and distribution sector reported thallium release to water less than 1 kg/year during the period (not shown in Figure 5-3). Thallium may end up in wastewaters from use and/or disposal of pharmaceuticals, from manufacturing dyes, fireworks, and wash off from chemical reactions (Couture et al. 2011). Releases of thallium were reported from only one wastewater treatment plant. The high levels of thallium reported from this facility in 2014 and 2015 were estimated using half the detection limit for non-detected measurements. In 2016, this plant removed thallium from their list of reportable substances, as there were "no results above the method detection limit (MDL) in two years" (NPRI 2017).
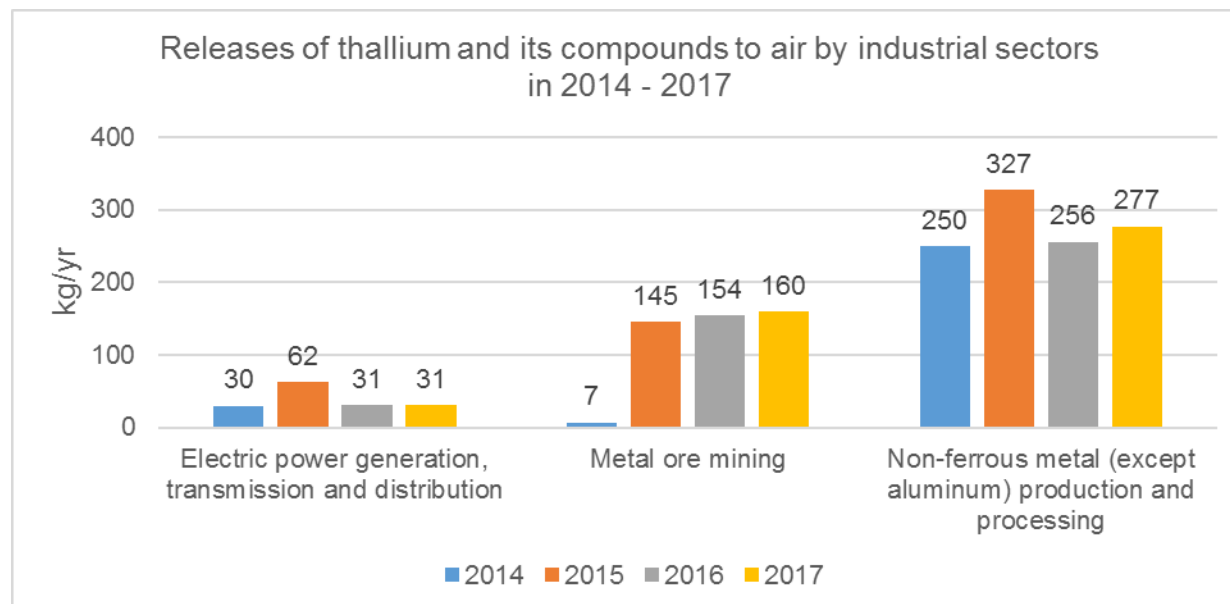
Figure 5-2. NPRI data on release of thallium and its compounds (kg/year) to air by industrial sectors in 2014 – 2017
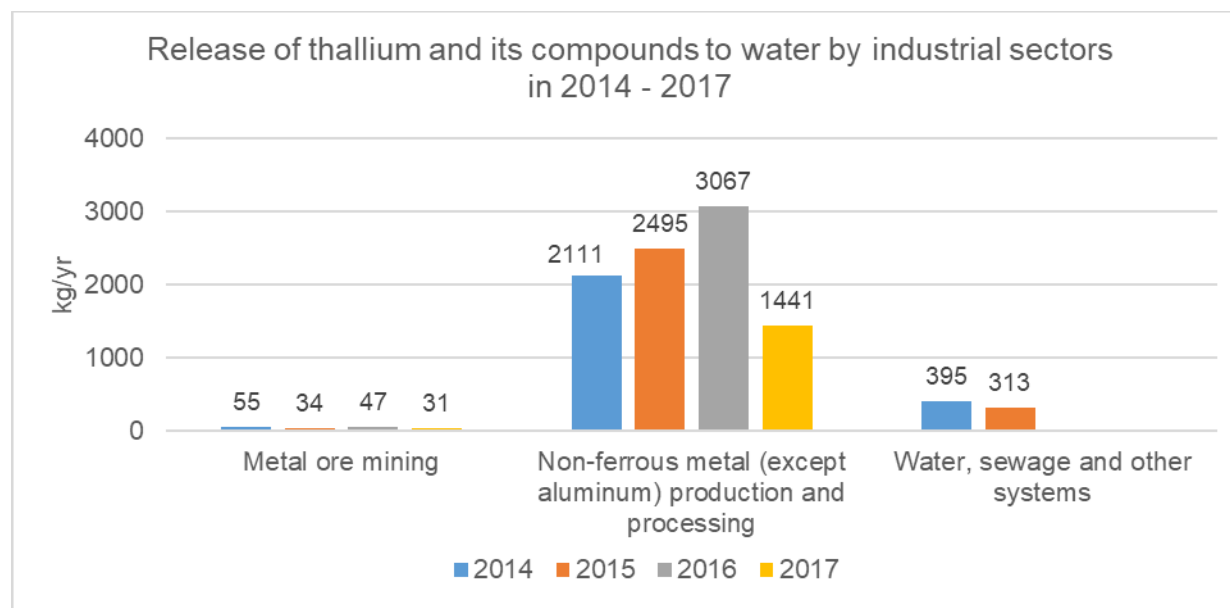
Figure 5-3. NPRI data on release of thallium and its compounds (kg/year) to water by industrial sectors in 2014 – 2017

In addition to the industrial sectors reported under NPRI, cement manufacturing production of potash fertilizer, petroleum refining, iron and steel production, and roasting pyrite during the production of sulphuric acid are other potential industrial processes that may also contribute to the release of thallium to the environment (Cheam 2001; IPCS 1996; McNeely et al. 1979; Schoer 1984), but thallium quantities involved are likely below the NPRI reporting threshold. Thallium can also leach out from decades-old accumulations of solid wastes from smelters, refineries, and gold-ore mills (Kazantzis

1979, 2000). Finally, thallium may also be present in municipal and industrial landfills due to historic use of thallium as pesticides/rodenticides (ATSDR 1992).

6. Environmental fate and behaviour

6.1 Environmental distribution

In air, thallium is removed by precipitation, atmospheric dispersion, and wet/dry depositions after entering the atmosphere (ATSDR 1992). Thallium emissions through atmospheric deposition have been traced in the Canadian Arctic ice and snow (Cheam et al. 2001), and are global in scope – for example, they have been reported in snow in Antarctica (Baiocchi et al. 1994; McConnell and Edwards 2008). Metallic thallium oxidizes slowly in air to form thallous oxide on the metal surface (Lee 1971). Photochemical reaction of thallium is not considered a significant fate process in the atmosphere (ATSDR 1992), even though thallous chloride is photosensitive (Cotton and Wilkinson 1980).

In the aquatic environment, thallium may exist in two oxidation states, monovalent thallous, Tl(I), and trivalent thallic, Tl(III) (Lan and Lin 2005). Tl(I) and Tl(III) differ significantly in terms of environmental mobility and toxicity. Tl(I) is the more thermodynamically stable form (Gao et al. 2007; Kaplan and Mattigod 1998; Lin and Nriagu 1998). According to Vink (1993), Tl(I) is the predominant form and is mobile when dissolved in water in the range of ~2 – 200 µg/L. Despite the fact that Tl(I) is the stable redox form of thallium in surface waters, Lin and Nriagu (1999) found that 70% of dissolved thallium in the Great Lake water is Tl(III). Twining et al. (2003) suggested that the reason for this may be a conversion of Tl(I) to Tl(III) by planktonic bacteria. Photooxidation of Tl(I) in the presence of aqueous cations (e.g., Fe(III) or As(V)) could also cause conversion of Tl(I) to Tl(III) in natural waters as demonstrated by Campanella et al. (2018). According to Cotton and Wilkinson (1988), Tl(III) is extensively hydrolysed and is dominated by inert $Tl(OH)_3$ complex which may precipitate, while the highly soluble and weakly reactive Tl(I) ion is the more bioavailable inorganic thallium species.

Thallium may also exist in the aquatic environment as stable organic dimethylthallium ion (DMT), $(CH_3)_2Tl^+$, which can be produced by biomethylating bacteria in anaerobic sediments as a detoxification mechanism (Huber and Kirchmann 1978). The biotic production of DMT in the ocean has also been reported (Schedlbauer and Heumann 2000). However, no measurement of DMT in fresh water has been made, nor is the aquatic toxicity of this thallium species known (Hassler et al. 2007; Schedlbauer and Heumann 2000). Considering that there is no known anthropogenic source of DMT, its environmental fate as well as ecotoxicity and bioaccumulation potential are not further considered in this screening assessment.

Thallium may partition from water to sediment and adsorb onto clay minerals, iron sulfide clusters, and hydrous metal oxides, e.g., manganese oxide (ATSDR 1992; Bidoglio et al. 1993; Callahan et al. 1979; Duan et al. 2012; Frantz and Carlson 1987;

Thomson et al. 1992; Zitko 1975). It is also suggested that the precipitation of Tl(III) hydroxide may be an effective mechanism for removing thallium from water, followed by reduction to Tl(I) by organic rich anaerobic sediment or bound to sediment with sulfide ion to form insoluble thallium(I) sulfide, Tl_2S (Gao et al. 2007; IPCS 1996; Laforte et al. 2005; Turner et al. 2010). The partition coefficients for suspended particles-water (log K_{pw}) of 4.28 and sediment-water (log K_{sw}) of 1.48 summarised by Harvey et al. (2007) indicate that thallium will be moderately mobile in sediment and highly adsorbent to particulate matter in surface water.

In soils, Tl(I) is considered to be the predominant form. Thallium in soils is generally adsorbed onto clays and colloids of manganese under reducing conditions (Kabata-Pendias and Pendias 1992). According to Bidoglio et al. (1993), thallium associates with Mn oxides/hydroxides resulting in surface oxidation of Tl(I) to Tl(III), which is then adsorbed or precipitated as Tl_2O_3. Some studies indicate that Tl sorption by iron oxides and soil organic matter is insignificant (Peter and Viraraghavan 2008; Vanek et al. 2015a, 2015b). Natural thallium contents in soil are predominantly represented by silicates and crystalline oxides with very low potential for thallium release and availability under common soil conditions (Vanek et al. 2009).

However, elevated thallium concentration in soils (through natural weathering of certain thallium-rich containing geological rocks/minerals) resulting in high plant accumulation have been reported in China and Czech Republic (Xiao 2004a; Pavlickova et al. 2005). Kabata-Pendias and Pendias (1992) also report that anthropogenic thallium in soils has been found to be very soluble thus readily available to plants. This is consistent with low reported soil-water partitioning coefficient value (logK_{ew}) of 0.68 reported by Harvey et al. (2007), indicating that thallium will be highly mobile in soil. In studying speciation of thallium in plants, Nolan et al. (2004) observed that Tl(I) was the only redox species of thallium to be accumulated in the leaves and was the most prevalent species in the *Iberis* intermedia plant.

6.1.1 Potential for long-range transport

The Long-Range Transport Potential (LRTP) was not estimated for this screening assessment, as inorganic substances are outside the domain of applicability of typical LRTP models. It is believed that thallium has a certain potential to travel long distance by air due to the mobility of thallium in fine particulate forms (ATSDR 1992). Environmental concentrations of thallium in environmental media and organisms in various remote, minimally exposed areas, such as the Canadian Arctic and other distant Arctic regions have been reported (Baiocchi et al. 1994; Cheam et al. 1996; Cheam 2001; Gantner et al. 2009). McConnell and Edwards (2008) presented a study based on continuous 1772 – 2003 monthly and annually averaged thallium deposition records from a Greenland ice core. The shift in thallium atmospheric deposition in the ice core was shown to correlate with the use of coal and/or oil and gas as primary fuel sources in North America and Europe.

6.2 Environmental persistence

Thallium metal oxidizes slowly in moisture and air (Lee 1971). Thallous chloride is photosensitive (Cotton and Wilkinson 1980), but no evidence indicates that thallium is transformed significantly by photochemical reactions in the atmosphere (Callahan et al. 1979).

Thallium as an element is persistent because it cannot be degraded further in the environment, although it can transform into different chemical species or partition among different phases within an environmental medium.

6.3 Potential for bioaccumulation

6.3.1 Bioavailability

Thallium is not an essential element for organisms. The assessment of thallium bioaccumulation in aquatic organisms should take into account the bioavailability of the redox species of thallium (Ralph and Twiss 2002). Twiss et al. (2004) presented the results of bioavailability of Tl(I) and Tl(III) in the unicellular algae *Chlorella sp.* and the diatom *Stephanodiscus hantzschii*. In their study, the concentration of free Tl(I) ion is close to the total dissolved Tl(I) concentration. Compared to Tl(I), the concentration of Tl(III) as free ion is extremely low and present mostly as inert Tl(OH)$_3$. Rickwood et al. (2015) also observed rapid conversion of Tl(III) to Tl(I) under laboratory conditions. As a result, the weakly reactive Tl(I) is considered the free thallium species in the aquatic environment at circumneutral pH (Ralph and Twiss 2002; Twiss et al. 2003).

In addition to how thallium speciation in environmental media affects its bioavailability and uptake, many studies have shown that dietary uptake also contributes to its accumulation by aquatic organisms (Lapointe and Couture 2009, 2010; Lapointe et al. 2009; Ouellet et al. 2013). Dietary thallium assimilation was found to be significant in juvenile fathead minnow compare to the fish at embryo/larvae stage (Lapointe and Couture 2009; Lapointe et al. 2010). The thallium uptake via water was more rapid than via diet when fish were exposed to water and diet simultaneously. Rapid induction of regulatory processes in fish gills limiting thallium uptake and accumulation, as well as activation of regulating mechanisms in fish gut to control diet-borne thallium uptake or elimination were reported (Lapointe and Couture 2009; Lapointe et al. 2010).

Thallium bioavailability to the soil-dwelling organisms and subsequent uptake by terrestrial plants is influenced by various factors. For plants, these factors are Tl speciation, type of soil (and, therefore, soil properties), Tl concentration in soil, plant species, and mobility of thallium in soil (Kazantzis 2000; Pavlickova et al. 2005; Vanek et al. 2015a, 2015b; Xiao et al. 2004b). Similar to the aquatic compartment, Tl(I) is the predominant form to be accumulated by plant root system from soil (Nolan et al. 2004;Tsakovski et al. 2006; Xiao et al. 2004b). Lukaszewski et al. (2018) investigated thallium mobility of the bottom soil samples (0.8–1.0 m deep) from over six different lithological backgrounds in Poland using a sequential extraction scheme. The authors

found that a significant percentage of thallium in most soil types is strongly entrapped in the aluminosilicate parent matter which represents immobile Tl form, thus not available for uptake by soil-dwelling organisms. The exception was for soil containing dispersed sulfide ores (Zn-Pb ores, pyrites, As-Sb ores) that are mobile in soils, suggesting thallium in soils of natural sulfide ores and anthropogenic sources of the same origin (metal ore mining, base smelters, etc.) is a significant resource of the most bioavailable Tl species for the uptake by terrestrial organisms.

6.3.2 Bioaccumulation in aquatic organisms

The bioconcentration factor (BCF) and bioaccumulation factor (BAF) approach for most metals is currently the object of numerous criticisms because these ratios are considered of little usefulness in predicting metal hazards (McGeer et al. 2003; Schlekat et al. 2007). Some metals may be accumulated because they are required as nutrients, or are partially detoxified internally. In addition, inverse relationships can occur for metal elements because metal accumulation by organisms generally follows saturation kinetics for which the metal uptake rate constant decreases with increasing concentration in the external medium (McGeer et al. 2003; Schlekat et al. 2007).

Borgmann et al. (2004) and Norwood et al. (2007) have developed a mechanistically-based saturation model to estimate metal BCFs or BAFs in the freshwater amphipod *Hyalella azteca* which avoids the above mentioned concentration dependence. In principle, organisms that do not store metals in detoxified forms may show a close relationship between BAFs and BCFs and chronic toxicity (Couillard et al. 2008). This approach has been validated in the field (Couillard et al. 2008), and is only applicable to sparingly essential and non-essential metals (e.g., thallium) but not physiologically regulated and nutritionally required metals. Field-derived BAFs are strongly correlated with the lab BCFs determined by the approach adopted by Borgmann et al. (2004) and Norwood et al. (2007) in Lake Ontario water. Table 6-1 lists empirical aquatic BCFs and BAFs produced for thallium using the approach of linking BCFs with chronic toxic effects for the freshwater amphipod *Hyalella azteca* (Borgmann et al. 1998; Borgmann et al. 2004; Couillard et al. 2008; Norwood et al. 2007).

Table 6-1. Empirical aquatic BCFs or BAFs produced for thallium for the freshwater amphipod *Hyalella azteca* (Borgmann et al. 1998; Borgmann et al. 2004; Couillard et al. 2008; Norwood et al. 2007)

Type of test [a]	Duration	Type of water	BCF or BAF (L/kg ww)
Field transplantation of *Hyalella azteca* in two rivers affected by metal mining in northwestern Québec (6 sites)	17 days	River waters (Allard River & Colombiere River)	1 645 [b]
Laboratory exposure	7 days	Lake Ontario water [c]	1 380 [b]
Laboratory exposure	7 days	Reconstructed water with no K$^+$	7 220 [b]

Abbreviations: ww: wet weight

[a] The freshwater amphipod *Hyalella azteca* was the test organisms in both field and laboratory studies.
[b] L/kg wet weight converted from dry weight using 0.19 g dry per 1 g wet.
[C] Water characteristics of Lake Ontario water used in the laboratory test: K^+ = 40 µM, hardness 130 mg/L, alkalinity 90 mg/L, pH 7.9-8.6

The protective effect of potassium (K) to Tl toxicity has been demonstrated for various aquatic organisms due to the well-known toxic mechanism for Tl to interfere with the vital K-dependent processes in living organisms (Borgmann et al. 1998; Hassler et al. 2007; Rickwood et al. 2015; Tatsi et al. 2015; Twiss et al. 2004). Increased K levels inhibit Tl accumulation in aquatic organisms and reduce Tl toxicity. This is further discussed in supporting documentation (ECCC 2018b).

Thallium concentrations in phytoplankton and macrophytes have been reported for few species, most of which were obtained in laboratory experiments. The field measurements by Zitko et al. (1975a) reported high thallium values in primary producers from rivers contaminated by mining activities in Canada. In particular, it was found that algae and mosses accumulated thallium up to 43.4 mg/kg dw and 162 mg/kg dw, respectively, at concentrations of Tl in water of 0.7 – 88.3 µg/L. The calculated mean BCF values were in the range of 908 – 1 895 L/kg dw for algae and 21 500 L/kg dw for moss. Higher field BCFs (~ 8 000 – 82 500 L/kg dw) were obtained by Quierolo et al. (2009) for two species of algae, *Myriophyllum acuaticum* and *Zannichelia palustris*, from water contaminated by processing of sulfide ores of copper, zinc and lead, and volcanic activity in northern Chile. Thallium concentration in algae was found to increase with time throughout the growth process (Quierolo et al. 2009).

Kwan and Smith (1988) studied toxicity and accumulation of Tl in *Lemna minor*. It was demonstrated that Tl uptake increased with exposure concentrations during 10-day laboratory tests. Plant BCF values were very high (6 000 000 – 88 000 000 L/kg), and the exposure concentrations displayed inverse relationships. The plants showed little or no recovery when moved to thallium free medium following exposure to 0.5 nmol/L (102 µg/L) and above. Threshold plant tissue concentrations for *Lemna* were in the range of 960 – 1 440 nmol/g (196 – 294 mg/kg), which was higher than the lethal body burden of ~300 nmol/g (62 mg/kg) derived from a 4-week study with *Hyalella* azteca (Borgmann et al. 1998).

Lapointe and Couture (2009, 2010) investigated thallium uptake via water and food by fathead minnow (*Pimephales promelas*) in the laboratory. Fish larvae accumulated considerably higher levels of thallium (up to 6.5 mg/kg dw) compared to juvenile fish (up to 0.052 mg/kg), but showed no effect on time to hatch, embryo survival, or enzyme activities. *Tubifex tubifex* were used as fish prey in both studies and exposed to thallium spiked sediment for 21 days. The calculated biota-sediment accumulation factors (BSAFs) were 0.92 – 1.32, similar to that of 0.47 – 1.44 reported for *Hyalella* (Borgmann et al. 1998).

Thallium is one of the trace metals monitored under the National Fish Contaminants Monitoring and Surveillance Program at ECCC (ECCC 2018). Three locations have been identified for the generation of Tl monitoring data for both water and fish body

concentrations under the program and federal/provincial water monitoring programs (ECCC 2018). One of the three locations identified with potential Tl enrichment from industrial impact included two water monitoring stations in the receiving waters, located approximately 5.6 and 13 km downstream from one of the facility's discharge points. The calculated geometric means of the measured Tl concentrations in water from 2005-2013 were 0.0242 µg/L and 0.00256 µg/L, respectively. Fish were also collected from the two water monitoring stations in multiple monitoring years during 2008 – 2015. The calculated geometric means of Tl whole body concentrations in rainbow trout and walleye were 0.110 mg/kg dw and 0.103 mg/kg dw, calculated field BAFs were 1 100 – 1 500 L/kg ww. The other two locations had very low measurable Tl concentrations in water in the range of below detection limit (DL at 0.001 – 0.1 µg/L) to 0.02 µg/L. The measured Tl whole body concentrations in fish were in the range of 0.0105 mg/kg dw – 0.0434 mg/kg dw, suggesting thallium can be accumulated by fish at very low concentrations in water. Field BAFs were not calculated for both locations because >80% of water Tl concentrations were below the detection limit.

Potential thallium contamination in the marine environment has been considered an emerging issue in industrialized areas. Fard et al. (2017) presented the mean concentration of thallium in Tonguefish muscle tissue at 0.781 mg/kg ww (0.984 mg/kg dw) and suggested a significant positive relationship between thallium concentration and fish length. Turner and Pillsburry (2013) fed marine snails with green macroalga (*Ulva lactuca*) and determined that only 2% thallium accumulated from sea water and 15% from diet, indicating dietary uptake was potentially more important than waterborne exposure. DelValls et al. (1999) reported that thallium levels in three estuarine/marine invertebrate species from an estuary contaminated by a mining spill were equal to or lower than in *Hyalella* from Lake Ontario (Borgmann et al. 1998). The calculated BSAFs were in the range of 0.25 – 1.93 at measured sediment concentration of 0.059– 0.080 mg/kg, comparable to the BSAFs for *Hyalella* and *Tubifex tubifex* (Borgmann et al. 1998; Lapointe and Couture 2009, 2010). Thallium levels in native clams and crabs as well as translocated oyster tissue were not increased significantly over 2 – 4 months of field study. Slightly increased thallium concentrations (0.07 – 0.20 mg/kg dw) were measured in mullet fish tissues (DelValls et al. 1999).

6.3.3 Bioaccumulation in terrestrial plants

Thallium uptake by plants is species-dependent, with *brassicaceae* family and *viola* species reported as the hyper-accumulators for thallium (Al-Najar et al. 2003; Antisari et al. 2016; Baceva et al. 2014; LaCoste et al. 2001; Leblanc et al. 1999; Pavlickova et al. 2005; Wang et al. 2013). Many studies (Al-Najar et al. 2003; LaCoste et al. 2001; Leblanc et al. 1999; Sun et al. 2012, 2015) suggested that the tolerance of some terrestrial plants toward thallium and its high accumulation in these plant species provides promising potential sources for bio- or phyto-remediation and phyto-mining in thallium-polluted areas.

Thallium levels in plants also directly reflect their immediate environment in the contaminated soil and accumulation of thallium in vegetation could increase with time throughout the growth process (Xiao et al. 2004b).

Thallium accumulation in certain parts of plants is also species-dependent. Queirolo et al. (2009) established that roots are the best accumulators for thallium with crops (potatoes, broad beans, and corn) collected near sites contaminated by copper mines, similar findings were also reported by Wierzbicka et al. (2004). However, field studies also showed the ability of certain plants to accumulate thallium and translocate the element into its aerial parts and reproductive tissues, indicating the capability of these plants to accumulate thallium in the above ground tissues (Antisari et al. 2016; Ferronato et al. 2016; Madejon 2013; Pavoni et al. 2017).

Fungi displayed a similar strain-dependant trend toward thallium accumulation. Urik et al. (2010) reported accumulation of thallium by a fungal strain up to 36 mg/kg and 430 mg/kg after exposure to thallium concentrations of 1.0 and 4.9 mg/L in cultivation media for 30 days. Fungal growth was reduced at both thallium concentrations after 10 days of exposure. Sun et al. (2012, 2015) demonstrated that some of the fungal strains can survive in thallium-contaminated soils and had high thallium biosorption and bioaccumulation ability.

6.3.4 Bioaccumulation in terrestrial animals

Similar to aquatic organisms, limited data was available on thallium bioaccumulation in terrestrial animals. Sager (1994) summarized that thallium accumulates primarily in liver, brain, and kidneys in terrestrial animals.

Dmowski et al. (1998) investigated small mammal populations in a community under conditions of extremely high thallium concentration near a Zn-Pb smelting and mining complex in the Bukowno-Olkusz region in Poland. Elevated thallium levels (up to 11 – 44 mg/kg) were detected in rodents' kidney and liver from two sites nearest the smelter. The site closest to the smelter and nearest to the slagheap had the highest contamination levels. One of the symptoms of thallium poisoning is progressive baldness or fur loss in animals: three unusual specimens with significant hair loss and pale fur were found among the captured rodents at the site nearest to the smelter. The whole small mammal community and adult mice productivity (population density, age structure) at the site was significantly reduced even compared to other zinc smelter/highly metal polluted sites. However, whether the observed effects to the rodents were indicative of potential chronic thallium toxicity alone could not be clearly identified as other trace metals from the smelter and slag could have also potentially contributed to the cause.

Other terrestrial animals at the same region were also monitored for thallium contamination by Dmowski et al. (1998, 2000, 2001, 2015). High concentrations of thallium were reported in the spawn, juveniles after metamorphosis, and in adult common toads (*Bufo bufo*), with the highest thallium levels found in the eggs (maximum

28 mg/kg). It was suggested that thallium in spawns was not absorbed from water (0.070 µg/L) or sediments (7.55 mg/kg dw) but was transferred directly from the females (Krasnodębska-Ostręga et al. 2005). The thallium concentrations in toads were much lower compared to wild vertebrates or birds of prey with symptoms of acute thallium poisoning (Clausen and Karlog 1974, 1977; Cromartie et al. 1975; Munch et al. 1974). The toads also displayed many characteristics demonstrating their adaptation to this adverse environment; no external developmental abnormalities in adult individuals, tadpoles, or juveniles from contaminated ponds were detected. There is a concern that the gelatinous egg masses or strings may be a significant thallium source for non-resident predators with no adaptation to high concentrations of thallium.

Sánchez-Chardi (2007) reported that Tl levels increased up to 3 – 10 times in liver and kidneys of the greater white-toothed shrew, *Crocidura russula*, in a mining spill contaminated site in Spain compared to the animals from the reference sites. Adults had higher Tl concentrations than juveniles, and females showed higher concentrations than males.

Chronic thallium accumulation by farm animals was investigated by Cwynar et al. (2014). Eight weeks of laying hen intoxication by food dosed with thallium caused accumulation in the tissues, internal organs, and eggs and its accumulation correlated with the feed levels and exposure duration. The highest thallium accumulations were found in the bones, followed by the kidneys, muscle and livers, indicating the easy absorption of this element by the gastrointestinal tract and its rapid distribution in the animal. No mortality of hens was observed but disorders in the homeostasis were observed at the highest dose of 16 mg/kg, effects including increased number of white blood cells, creatinine, hematocrit, and the decrease in blood glucose levels. The increase in serum creatinine suggests that the high levels of thallium in kidneys may contribute to impaired renal filtration processes reducing thallium elimination from the body and leading to further accumulation.

The main metal source for aquatic birds is their diet. Higher thallium levels were reported for eight duck species in contaminated sites compared to the birds from the reference (uncontaminated) sites in Japan by Mochizuki et al. (2005). No ducks from contaminated sites in the study indicated toxic physical effect. Benito et al. (1999) reported monitoring data on trace elements in the blood of aquatic birds after mining spill in wetlands of a national park in Spain, but found that thallium was not present in birds at any significant concentration (Tl concentrations were below DL of 2 µg/L).

6.3.5 Biomagnification potential

Animals living in areas of metal contamination, or that readily feed on organisms vulnerable to metal accumulation are at a particular risk for accumulation themselves. This seems to be the case in lower trophic level organisms as they tend to have large quantities of extremely polluted medium in their digestive tracts, and are then consumed by higher trophic level organisms, leading to biomagnification. The research on thallium biomagnification potential, however, is limited and results are at times contradictory.

Thallium has been found to potentially biomagnify in the food chain of an isolated arctic lake dominated by arctic char (Gantner et al. 2009). Lake Hazen is the largest lake in the Canadian high arctic with little anthropogenic contamination and has been used for a mercury bioaccumulation study. Thallium concentrations in char muscle tissue were examined with mercury as an indicator. Thallium showed a direct relationship to char's trophic position as identified by $\delta^{15}N$[6], indicating the potential to biomagnify. A similar trend was reported by Lin et al. (2001) which measured thallium concentrations in adult lake trout from Lake Michigan. A correlation was found between trout growth factor (fish weight/age) and thallium concentration.

In aquatic food chains, freshwater invertebrates and fish take up thallium present in their food (Couture et al. 2011). The degree to which elements such as thallium transfer from one trophic level to the next is a function of their assimilation efficiency. For a given trace element, its assimilation efficiency depends on several factors including the availability of the element in the food particles and the digestive physiology of the predator (Couture et al. 2011). Fractionation techniques measuring the distribution of thallium among prey cell fractions were used to illustrate the likelihood of thallium availability for uptake and subsequent assimilation by predators (Dumas and Hare 2008; Lapointe and Couture 2009; Lapointe et al. 2009; Smith and Kwan 1989). In general, trace metals present in the cytosol and the organelle fractions of prey that are readily assimilated by predators are referred to as trophically available metals (Wallace and Luoma 2003). Thallium is normally found in the cytosol of aquatic invertebrates, juvenile fish, and plants (25 – 85%), and thus can be readily assimilated by predators or grazers. The reported trophically available thallium in aquatic organisms ranged from 50% in *D. magna* and *T. tubifex* by fathead minnow (Lapointe et al. 2009) to 75% in *C. riparius* by the alderfly (Dumas and Hare 2008), suggesting potential trophic transfer along aquatic food chains. Figure 6-1 illustrates the assimilation efficiency with which thallium is transferred among trophic levels in planktonic and benthic food webs (Couture et al. 2011; Dumas and Hare 2008; Lapointe and Couture 2009; Lapointe et al. 2009; Twining and Fisher 2004).

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[6] $\delta^{15}N$ is the stable nitrogen isotope signatures; they have been increasingly used in the past to infer the trophic position of consumers in food web studies. Interpreting the stable nitrogen isotope signatures ($\delta^{15}N$) of consumers relative to the $\delta^{15}N$ characterizing the food-web base provides a time-integrated measure of trophic position.
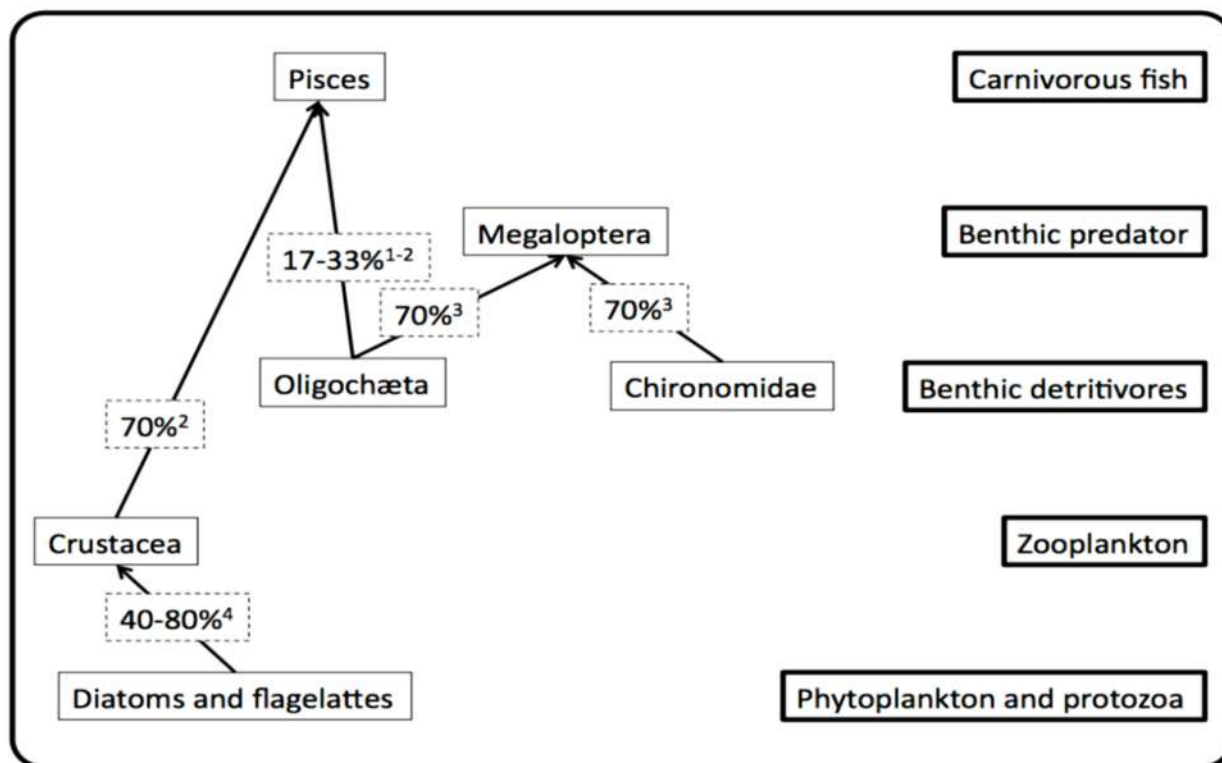
Figure 6-1. Schematic diagram illustrating the assimilation efficiency of thallium transfer among trophic levels in planktonic and benthic food webs (Couture et al. 2011).

However, contradictory observations were also reported for potential thallium biomagnification in aquatic or terrestrial food chains. No evidence of biomagnification of thallium was observed in field studies of various aquatic food webs (Ikemoto et al. 2008; Ofukany et al. 2014; Twiss et al. 2003) and invertebrate sub-populations (Dmowski and Badurek 2001).

Therefore, the present weight of evidence indicates that thallium, released to the environment via both natural and anthropogenic sources in its bioavailable forms, maybe accumulative in both aquatic and terrestrial organisms. Aquatic and terrestrial organisms exposed to thallium in their habitats readily take up thallium by direct contact with environmental media and/or by food ingestion with uptake through the gastrointestinal tract (Couillard et al. 2008; Ecoscape Environmental consultants Ltd. and Larratt Aquatic Consulting Ltd. 2014; Kazantzis 2000; Lapointe and Couture 2009, 2010; Lapointe et al. 2009; Lin et al. 2005; Ouellet et al. 2013; Pavlickova et al. 2006; Vanek et al. 2015a,b; Xiao et al. 2004b). Considerably elevated thallium concentrations in the vicinities of point source areas (e.g., smelters) may have an impact to organisms living in such an environment (Dmowski et al.1998, 2000, 2001, 2015). However, essential information is lacking to quantify the level of thallium tissue residue concentrations associated with adverse effects (e.g., effect vs. critical body/tissue

burden, chronic effects in subcellular level), as well as the thallium detoxification mechanisms and routes by various receptors in the environment.

No conclusion can be reached on the potential of thallium biomagnification in both aquatic and terrestrial food chains considering the limited and contradictory data currently available. The subcellular studies suggested potential thallium assimilation from lower trophic levels to higher trophic levels in aquatic food chains (Dumas and Hare 2008; Lapointe and Couture 2009; Lapointe et al. 2009; Smith and Kwan 1989). However, contradictory information from the field biomagnification studies warrant further research in identifying appropriate predator-prey relationships and examination on thallium transfer among larger varieties of prey-predator food chains in the environment.

7. Potential to cause ecological harm

7.1 Ecological effects assessment

7.1.1 Mode/mechanism of action

The exact mechanism of thallium toxicity is still under investigation. The most well known mechanism of thallium toxicity is related to its interference with the vital potassium-dependent processes in both aquatic and terrestrial organisms. Having similar ionic charges and radii, thallus ion Tl(I) can mimic the biological action of potassium ions due to the cell membrane's inability to distinguish between thallium and potassium. In certain living systems, Tl(I) has greater affinity (~ 10 times) for uptake than K^+ in the (Na,K)-ATPase membrane porters (Brismar 1998). By mimicking potassium in its movement and intracellular accumulation in mammals, Tl(I) interferes competitively with some potassium-dependent biological reactions. Thallium has been shown to replace potassium ion in the activation of several monovalent cation-activated enzymes, e.g., pyruvate kinase, ATPase, and aldehyde dehydrogenase. Thallium has also been found to replace potassium in the stabilization of ribosomes, and in physiological functions such as muscle contraction (ATSDR 1992; Galvan-Arzate and Santamaria 1998; IPCS 1996).

Like other metals, thallium has a high affinity for sulfhydryl groups of proteins and mitochondrial membranes inhibiting a range of enzyme reactions and leading to a generalized poisoning (Ramsden 2002). Thallium forms ligands with protein sulfhydryl groups inhibiting cellular respiration, interacts with riboflavin and riboflavin-based cofactors, and distribution of calcium homeostasis (Mulkey and Oehme 1993). Thallium can also influence enzyme production and amino acid synthesis, affect transport mechanisms, and cause reduction of mitosis (Schoer 1984).

Siegel and Siegel (1975) discovered that a high thallium concentration (10 mM Tl) may induce potassium deficiency in cucumber seedlings. They also found that thallium is more disruptive to mechanisms associated with cell multiplication than cell growth or differentiation (Siegel and Siegel 1975). Scheckel et al. (2004) discovered that the

majority of thallium distributed in the veins of *Iberis* plant (*Brassicaceae* family) was free Tl(I) ion within the vascular system but not accumulated in the mesophyll and stomatal cells to disrupt photosynthesis or water regulation. In corn and sunflower plants, however, thallium was found to accumulate in the guard cells, which could cause reduced photosynthesis (Carlson et al. 1975). Recent studies of *Lemna minor* plants exposed to Tl(I) reported that thallium interfered with molecular and enzymatic antioxidant protective mechanisms (Babic et al. 2009; Radic et al. 2009). The thallium-induced oxidative stress was characterized by increased production of reactive oxygen species, and could also be an important mechanism of thallium toxicity (Radic et al. 2009). Pu et al. (2017) suggested that the accumulation of Tl in a perennial tropical plant *Coix lacryma-jobi* (*Poaceae* family) inhibited photosynthesis (namely, the photo-activation of Photosystems II[7]). The toxic effects of Tl triggered activation of the antioxidant systems (i.e., catalase and peroxidase) in the plant which moderated the adverse effects of Tl.

Fish regulate thallium uptake from water via their gills and diet uptake via the gut. The regulation of thallium could be related to K homeostasis in the epithelial cells (Lapointe and Couture 2009). Hou et al. (2017) exposed adult female zebrafish to environmentally -relevant concentrations of thallium (0.02 – 1 µg/L) for 96 days and demonstrated that Tl induced a number of biochemical alterations and histological lesions in fish gill, liver, and gonad tissues. A subcellular examination suggested that thallium may cause oxidative stress in zebra fish.

Belowitz (2014) examined the mechanism of Tl(I) toxicity to the larval form of a comparatively thallium-tolerant non-biting midge *Chironomus riparius* and suggested that the possible mechanisms of thallium detoxification involves excretion of Tl(I) by the renal tubules of the midge or by binding sulfur-rich proteins such as metallothionein that render Tl(I) inert.

7.1.2 Toxicity modifying factors (TMFs)

Some available data, albeit limited, suggest that potassium is able to effectively reduce Tl(I) toxicity in aquatic organisms, thereby being a potential TMF for thallium (ECCC 2018b); however, this cannot be reliably confirmed using statistical analyses. Therefore, applying potassium as a TMF for freshwater PNEC derivation will not be considered in this assessment.

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[7] Photosystem II (or water-plastoquinone oxidoreductase) is the first protein complex in the light-dependent reactions of oxygenic photosynthesis.

7.1.3 Effects on aquatic organisms

Thallium toxicity is not as extensively studied as other inherently toxic elements with similar toxicity such as lead, mercury and cadmium.

Based on the speciation and bioavailability of the two thallium redox forms (see Section 6.1 of this report), Tl(I) is the focus of this ecological effects assessment to evaluate the toxicity of the thallium moiety. It has been shown that the proportion of free Tl(I) is in close proximity to the total dissolved Tl(I) concentration in the aquatic environment due to its low affinity to ligands to form complexes (Lan and Lin 2005; Lin and Nriagu 1998; Ralph and Twiss 2002). Rickwood et al. (2015) also found that Tl(I) was stable, whilst Tl(III) was converted to Tl(I) under experimental conditions during toxicity tests of up to 21 days (Rickwood et al. 2015).

Acute toxicity data for thallium to freshwater organisms were compiled and critically reviewed (Nautilus Environmental 2016). Toxicity endpoints and values (from reliable studies) that met the requirements for derivation of a short-term Type A Canadian Water Quality Guideline (CCME 2007) were summarized in Appendix A (Table A-1). These data were used to develop a short-term species sensitivity distribution (SSD) using the software SSD Master Version 3.0 (SSD Master 2013) (Figure 7-1). When more than one acceptable endpoint was available for a certain individual species, the geometric mean was calculated in accordance with the preferred endpoint guidance of the CCME (2007) protocol.

Bluegill (*Lepomis macrochirus*) and Harlequin fly (*Chironomus riparius*) are the more tolerant species with 96h LC_{50} above 100 000 µg/L (Table A-1). With the exception of the two tolerant species, other freshwater organisms demonstrated a relatively similar range (LC_{50} values of 12 – 7 680 µg/L) of sensitivity to the toxic effects of Tl (Table A-1). According to the CCME protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic life (CCME 2007), algae toxicity tests with exposure periods less than 24h with severe effects are generally considered in short-term datasets due to their rapid cell division rate. However, the 48h LC_{50} for algae growth was selected due to the growth lag observed in control cultures at 24h (Tatsi 2017, personal communication, not referenced).
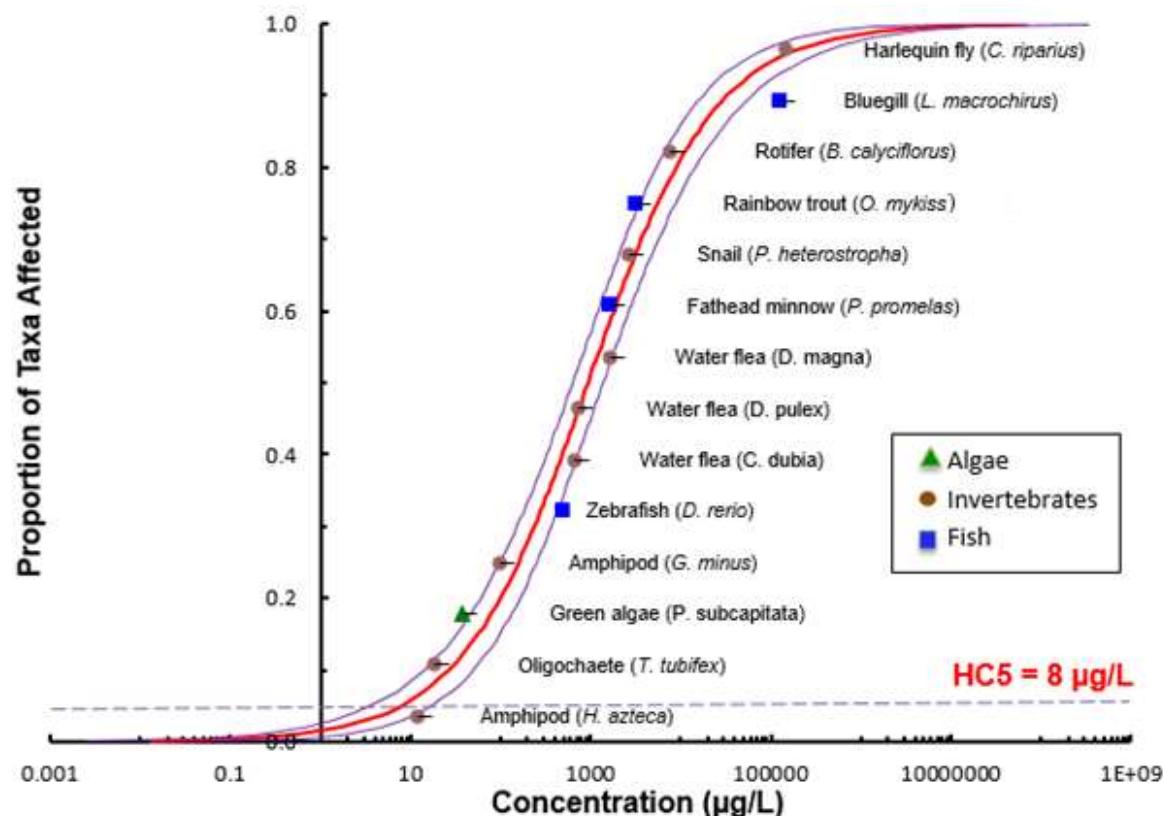
Figure 7-1. Species sensitivity distribution (SSD) for short-term thallium freshwater toxicity.

Model assumptions and fit were verified with statistical tests when deriving the SSD. The logistic model provided the best fit of the models tested. The 5th percentile (HC$_5$), i.e., hazardous concentration to 5% of freshwater species, of the SSD plot was 8 µg/L (Figure 7-1). The HC$_5$ of 8 µg/L calculated from the SSD is selected as the critical toxicity value (CTV) for short-term thallium freshwater toxicity.

Table 7-1 summarizes reliable chronic toxicity data for freshwater organisms for Tl. As shown with acute tolerance to Tl toxicity (with the exception of bluegill and harlequin fly), freshwater organisms also demonstrated relatively similar ranges (i.e., LOEC and E(I)C$_{10-25}$ effect values of 1.8 – 806 µg/L) of long-term sensitivity to the toxic effects of Tl. The dataset for thallium toxicity is not adequate for a long-term SSD approach due to the lack of reliable chronic toxicity studies and applicable chronic toxicity data on fish and invertebrate species (Table 7-1) as specified in the CCME protocol (2007).

Table 7-1. Reliable chronic aquatic toxicity studies for freshwater for thallium

Common name	Test organism	Endpoint	Value (µg/L) [a]	Reference
Fish	Fathead minnow (*Pimephales promelas*)	28 d EC$_{10}$ length	688	Kimball 1978

Common name	Test organism	Endpoint	Value (µg/L) [a]	Reference
Fish	Fathead minnow (*Pimephales promelas*)	28 d EC_{10} weight	806	Kimball 1978
Fish	Fathead minnow (*Pimephales promelas*)	30 d EC_{10} length	79.2	LeBlanc & Dean 1984
Fish	Fathead minnow (*Pimephales promelas*)	30 d EC_{10} weight	69.2	LeBlanc & Dean 1984
Fish	Fathead minnow (*Pimephales promelas*)	7 d IC_{25} weight	201 (235.8)	Rickwood et al. 2015
Fish	Fathead minnow (*Pimephales promelas*)	21 d LOEC reproduction	8	Rickwood et al. 2015
Fish	Fathead minnow (*Pimephales promelas*)	21 d NOEC reproduction	0.8	Rickwood et al. 2015
Invertebrates	Amphipod (*Hyalella azteca*)	4 wk LC_{25}	2.5	Borgmann et al. 1998
Invertebrates	Amphipod (*Hyalella azteca*)	6 wk EC_{25} growth	1.8	Borgmann et al. 1998
Invertebrates	Water flea (*Ceriodaphnia dubia*)	7 d IC_{25} reproduction	100	Pickard et al. 2001
Invertebrates	Water flea (*Ceriodaphnia dubia*)	7 d IC_{25} reproduction (K^+ depleted)	35.01	Rickwood et al. 2015
Invertebrates	Water flea (*Ceriodaphnia dubia*)	7 d IC_{25} reproduction	160 – 189	Rickwood et al. 2015
Plants	Duckweed (*Lemna minor*)	7 d EC_{10} frond number	142	Naumann et al. 2007
Plants	Duckweed (*Lemna minor*)	7 d EC_{10} fresh weight	114	Naumann et al. 2007
Plants	Duckweed (*Lemna minor*)	7 d EC_{10} dry weight	153	Naumann et al. 2007
Plants	Duckweed (*Lemna minor*)	7 d EC_{20} frond number	202	Naumann et al. 2007
Plants	Duckweed (*Lemna minor*)	7 d EC_{20} fresh weight	150	Naumann et al. 2007
Plants	Duckweed (*Lemna minor*)	7 d EC_{20} dry weight	210	Naumann et al. 2007

Common name	Test organism	Endpoint	Value (µg/L) [a]	Reference
Plants	Duckweed (*Lemna minor*)	7 d EC_{20} growth rate	202	Henke et al. 2011
Algae	Algae (*Selenastrum capricornutum*)	72 h IC_{25} growth	90	Pickard et al. 2001
Algae	Algae (*Pseudokirchneriella subcapitata*)	72 h EC_{25} growth	40	Tatsi et al. 2015
Algae	Algae (*Pseudokirchneriella subcapitata*)	72 h EC_{25} yield	17	Tatsi et al. 2015
Algae	Algae (*Pseudokirchneriella subcapitata*)	72 h EC_{25} growth (K^+ depleted)	4.6	Rickwood et al. 2015
Algae	Algae (*Pseudokirchneriella subcapitata*)	72 h EC_{25} growth	160 – 182	Rickwood et al. 2015

[a] The toxicity endpoints listed are for Tl(I). If the thallium speciation was not specified in the study, it was assumed to be Tl(I). Endpoints were converted to µg/L if original data was reported in mg/L.

The thallium chronic PNEC was therefore derived by using the SSD-derived short-term CTV for thallium freshwater toxicity and applying an assessment factor (AF) of 10 to extrapolate for the short to long-term exposure duration, mortality to sub-lethal effects and median to low- or no-effect (Environment Canada 2013). The resulting chronic PNEC$_{freshwater}$ is 0.8 µg/L for thallium.

Chronic PNEC$_{freshwater}$ = short-term CTV ÷ AF = 8 µg/L ÷ 10 = 0.8 µg Tl/L

The PNEC$_{freshwater}$ of 0.8 µg/L was compared to the reliable thallium chronic toxicity endpoints (Table 7-1) as a precaution so that the organisms are adequately protected from thallium toxicity over long-term exposure. *Hyalella azteca* is the most sensitive freshwater species tested (Table 7-1) with 4 week LC_{25} at 2.5 µg/L and 6 week growth effect EC_{25} at 1.8 µg/L. Rickwood et al. (2015) performed a 21-day adult fathead minnow reproductive test at thallium concentrations of 8 µg/L and 0.8 µg/L (Table 7-1). Reduced reproductive effects (i.e., cumulative spawning) were observed in the 8 µg/L thallium treatments but not in the 0.8 µg/L treatments, suggesting that the long-term freshwater PNEC of 0.8 µg/L is protective.

The thallium PNEC for freshwater organisms is the same as the long-term water quality thresholds suggested by CCME (1999): 0.8 µg/L.

There is limited information regarding ecotoxicological effects of thallium in marine water (Table 7-2). It is suggested that the low thallium (ng/L) and high potassium contents in seawater should reduce thallium uptake and toxicity to marine organisms, but high phytotoxicity was observed in certain marine species. Turner and Furniss

(2012) investigated toxicity and bioaccumulation of thallium in the marine macroalga (*Ulva lactuca*). The green macroalga showed a high phytotoxicity with 48h LOEC at 10 µg/L in both coastal seawater and estuarine water. Statistical analysis was not performed by the author, the 48h EC_{50} of 20 and 23 µg/L were estimated via US EPA TRAP program with the figure provided for the macroalga 48h exposure in sea water (salinity of 33) and estuarine water (salinity of 20), respectively (Turner and Furniss 2012). The toxicity of Tl to marine algae is in a similar range as the toxicity value shown for freshwater algae (i.e., 48h EC_{50} of 37 µg/L), albeit marine algae is more sensitive to the toxic effects of Tl. The toxicity is suggested to be associated with thallium uptake through the cell membrane via coupled NaCl/KCl transport, the uptake rate rising with increasing concentrations of both Na^+ and Cl^- (Turner and Furniss 2012). While rotifer (*Brachionus plicatilis*) is the least sensitive crustaceans to thallium effect with 24 h LC_{50} at 100 000 µg/L, the toxicity values for other marine invertebrate species are 3-25 times lower (LC_{50} values of 2 400 – 32 300 µg/L). The available thallium acute toxicity data to marine fish species fall in a very narrow range of 21 000 – 24 000 µg/L (Table 7-2). The marine invertebrates and fish showed similar or slightly higher tolerance to the toxic effects of Tl compared to the freshwater organisms (Table A-1).

The dataset for marine water toxicity is not adequate (minimum data requirements are not met according to CCME 2007) for an SSD approach to derive the CTV. Therefore, an assessment factor approach was used. The most sensitive value, the 48h EC_{50} of 20 µg/L with macroalga (*Ulva lactuca*) in costal seawater is selected as the CTV for thallium toxicity in marine water). The CTV is further divided by an assessment factor of 5 to extrapolate from median to low-level effects and a further assessment factor of 5 to account for the specific mode of action (i.e., phytotoxicity in marine macroalga). The resulting chronic $PNEC_{marine\ water}$ is 0.8 µg/L.

Chronic $PNEC_{marine\ water}$ = CTV ÷ AF = 20 µg/L ÷ 5 ÷ 5 = 0.8 µg Tl/L

The identical chronic PNEC values derived for fresh and marine water organisms suggested that thallium exerts similar level of toxicity to the most sensitive aquatic organisms (Table A-1 and 7-2), thus a unified chronic $PNEC_{water}$ of 0.8 µg/L is applied for Tl.

Table 7-2. Key toxicity studies considered in choosing a critical toxicity value for marine water for thallium

Common name	Test organism	Endpoint	Value (µg/L) [a]	Reference
Fish	Sheepshead minnow (*Cyprinodon variegatus*)	96 h LC_{50}	21 000	Heitmuller et al. 1981
Fish	Silverside (*Menidia menidia*)	96 h LC_{50}	24 000	Dawson et al. 1976
Invertebrates	Brine Shrimp (*Artemia salina*)	48 h LC_{50}	10 700	Onikura et al. 2008

Invertebrates	Brine Shrimp (*Artemia salina*)	24 h LC$_{50}$	32 300	Calleja et al. 1994
Invertebrates	Mysid shrimp (*Americanmysis bahia*)	96 h LC$_{50}$	3 480	Onikura et al. 2008
Invertebrates	Rotifer (*Brachionus plicatilis*)	24 h LC$_{50}$	100 000	Onikura et al. 2008
Invertebrates	Copepod (*Acartia tonsa*)	96 h LC$_{50}$	2 400	Horne et al. 1983
Invertebrates	Amphipod (*Gammarus annulatus*)	96 h LC$_{50}$	4 200	Horne et al. 1983
Invertebrates	Sand shrimp (*Crangon septemspinosus*)	96 h LC$_{50}$	2 500	Horne et al. 1983
Invertebrates	Grass shrimp (*Palaemonetes pugio*)	96 h LC$_{50}$	5 600	Horne et al. 1983
Invertebrates	Polychaete (*Neanthes arenaceodentata*)	96 h LC$_{50}$	17 000	Horne et al. 1983
Algae	Green macroalga (*Ulva lactuca*)	48 h LOEC	10	Turner and Furniss 2012
Algae	Green macroalga (*Ulva lactuca*)	48 h LC$_{50}$	20 [b]	Turner and Furniss 2012
Algae	Green macroalga (*Ulva lactuca*)	48 h LC$_{50}$	23 [b]	Turner and Furniss 2012

[a] The toxicity endpoints listed are for Tl(I). If the thallium speciation was not specified in the study, it was assumed to be Tl(I). Endpoints were converted to µg/L if original data was reported in mg/L.
[b] The values are estimated with US EPA TRAP program.

7.1.4 Effects on sediment organisms

Although the ecotoxicity data for thallium in sediments is very scarce and insufficient to derive a PNEC for that medium, some relevant information can be found in the scientific literature. For example, Borgmann et al. (1998) studied thallium chronic toxicity to *Hyalella* in tap water (coming from Lake Ontario) and an artificial sediment without adding potassium and derived the lethal body concentration resulting in 25% mortality (LBC$_{25}$) based on the calculated thallium uptake by the organism versus thallium concentration in water (BCF). A 4-week LBC$_{25}$ of 290 nmol/g (59 mg/kg) was calculated combining all *Hyalella* tests. Thallium concentrations in *Hyalella* collected from six sites in Hamilton Harbour and Lake Ontario sediments were analyzed and the maximum level of Tl accumulated by the organism from the surrounding sediments was 4.9 nmol/g (1.0 mg/kg), equivalent to ~ 2% of the 4 week LBC$_{25}$, suggesting Tl levels at 0.53 – 4.2 nmol/g (0.11– 0.86 mg/kg) in sediments were unlikely to cause adverse environmental effects to the organism (Borgmann et al. 1998).

7.1.5 Effects on soil-dwelling organisms

There is limited information regarding ecotoxicological effects of thallium in soils. Anthropogenic thallium in soils has been shown to be very soluble and readily available

to plants (Schoer 1984; Kabata-Pendias and Pendias 1992). Adverse effects to plants have been reported at concentrations as low as 1 mg/kg of dry plant tissue (IPCS 1996). The Canadian soil quality guideline for long-term exposure to soil organisms is 1 mg/kg dw (CCME 1999), based on reported thallium LOEC values to terrestrial plants and invertebrates (McCool 1933; Lachover et al. 1958; Environment Canada 1996, 1998). The guideline value corresponds to the upper 98th percentile value of the range of typical concentrations of thallium in Ontario soils (CCME 1999).

Heim et al. (2002) reported soil bioassay studies with plants and terrestrial invertebrates. Reproduction of terrestrial invertebrates is more sensitive than growth and mortality to thallium in soil. Adverse effects for the hatching of land snails (*Arianta arbustorum*) and reproduction of earthworms (*Eisenia fetida*) were observed in soils with thallium concentrations of 1 mg/kg and 5 mg/kg, respectively. The growth and survival of the snails and the earthworms are more tolerant endpoints with reported 4-week LOECs in the range of 100 mg/kg to 500 mg/kg. The 7-d LOECs for garden cress (*Lepidium sativum*) seedlings were reported at 10 mg/kg for shoot growth and 100 mg/kg for root growth in the same study.

Fischer and Molnar (1997) reported that 1 mM/kg of TlCl (204 mg Tl/kg) resulted in an initial mass gain followed by marked mass loss and mortality to the earthworms (*Eisenia fetida*) after 2 weeks of exposure and only 15% survival of the earthworms after 7 weeks of exposure.

Current information available for thallium soil toxicity indicates that a $PNEC_{soil}$ set at 1 mg/kg dw (dry weight) in soil, as per the 1999 CCME guideline, is protective for soil dwelling organisms and plants in the Canadian environment.

7.2 Ecological exposure assessment

7.2.1 Natural background concentrations

Thallium is ubiquitous in the environment, and in some areas of Canada, which are not impacted by anthropogenic activities (i.e., areas representative of background conditions), concentrations of thallium may be naturally elevated. In other areas, anthropogenic activities cause thallium concentrations to be higher than background concentrations.

Background concentration ranges, or normal ranges, of total thallium in surface waters for Canadian ecozones were recently estimated by Kilgour & Associates Ltd. (2016). Median background concentrations of thallium for Canadian ecozones were calculated using the approach from Kilgour & Associates Ltd. (2016) from reference samples, deemed as such by the approach outlined in Proulx et al. (2018), from a variety of federal and provincial surface water quality monitoring programs and other

repositories[8]. Median concentrations of thallium are also available for Lake Erie, Lake Ontario, and Lake Superior using measurements taken during the period of 2005 to 2015[9]. In all cases, analytically non-detectable concentrations were substituted with the ½ DL (detection limit) values. The median thallium concentration (total or dissolved) for all regions in Canada is in the range of 0.002 – 0.05 µg/L (Table 7-3), being similar to the freshwater Tl concentrations of 0.005 – 0.01 µg/L estimated by Reimann and Caritat (1998). Higher thallium concentrations (max. 4.4 µg/L) were detected in the Boreal Plain and Prairies ecozones where natural weathering of sedimentary bedrocks may contribute to the higher thallium concentration. Median concentrations of thallium were also calculated for the Great Lakes (except Lake Michigan) using data collected during 2005-2015 by the Water Quality Monitoring and Surveillance group of ECCC. Concentration ranges of 0.001 – 0.009 µg/L of mean total dissolved thallium concentration (Table 7-3) are in reasonable agreement with what was reported for the Great Lakes by Cheam (1995, 2001).

Table 7-3. Total thallium concentrations for Canadian Ecozones and the Great Lakes

Region	Sample size (% detection)	Range of Tl (µg/L)	Median of Tl (µg/L)
Boreal Shield	159 (0%)	< 0.01 - < 0.06	0.05
Atlantic Maritime [a]	2 (0%)	< 0.1	0.05
Boreal Plain	629 (51%)	< 0.0003 - 4.4	0.05
Prairie	411 (88%)	< 0.01 - 1.03	0.05
Taiga Cordillera	4 (n/a)	0.002 - 0.066	0.006
Boreal Cordillera	286 (n/a)	0.0005 - 0.164	0.003
Pacific Maritime	1 322 (13%)	< 0.001 - 0.239	0.002
Montane Cordillera	1 336 (8.8%)	< 0.001 - 0.058	0.003
Lake Superior	83 (93%)	0.0005 - 0.007 (DL 0.001)	0.001
Lake Superior [b]	- [c]	- [c]	0.001
Lake Huron	80 (100%)	0.002 - 0.013 (DL 0.001)	0.004
Lake Huron [b]	- [c]	- [c]	0.010
Lake Erie	106 (100%)	0.004 - 0.052 (DL 0.001)	0.009
Lake Erie [b]	- [c]	- [c]	0.009

[8] BQMA 2015; FQMS 2014; FQMS 2016; NLTWQM 2016; PWQMN 2015; RAMP 2016; personal communication, data prepared by the Water Stewardship Division, Province of Manitoba, for the Ecological Assessment Division, Environment and Climate Change Canada, dated February 24 2016; unreferenced; personal communication, data prepared by the Environmental and Municipal Management Services, Saskatchewan Water Security Agency, for the Ecological Assessment Division, Environment and Climate Change Canada, dated February 25 2016; unreferenced

[9] Personal communication, data provided by the Water Quality Monitoring and Surveillance Division, Environment and Climate Change Canada (ECCC) for the Ecological Assessment Division, ECCC, dated June 20 2017; unreferenced

Region	Sample size (% detection)	Range of Tl (µg/L)	Median of Tl (µg/L)
Lake Ontario	165 (100%)	0.003 - 0.059 (DL 0.001)	0.007
Lake Ontario [b]	- [c]	- [c]	0.006
Lake Michigan [b]	- [c]	- [c]	0.014

Abbreviations: n/a = not available
[a] Total thallium concentrations are unavailable for the Atlantic Maritimes and therefore dissolved thallium median concentrations are reported.
[b] Cheam 2001, unit converted from pmol/L.
[c] Information not available.

Limited information is available for thallium concentrations in Canadian soils. OMEE (1993) reported the 98th percentile concentrations of 0.81 mg/kg and 0.77 mg/kg for rural parkland and old urban parkland in Ontario, respectively. A median thallium soil concentration in Canada of 0.5 mg/kg was estimated by Reimann and Caritat (1998). A recent review suggested average background thallium concentrations of 0.20 – 0.82 ppm in soils around the world (Belzile and Chen 2017).

The natural content of thallium in plants of approximately 0.05 mg/kg and less than 0.1 mg/kg dry weight were reported by Krasnodebska-Ostrega and Golimovski (2008) and by Geilmann et al. (1960). In plant ash, Tl concentrations of 1 mg/kg were reported (Dvornikov et al. 1973, 1976).

7.2.2 Approach for the exposure characterization

Detailed exposure scenarios were developed for the three sectoral activities that result in the highest releases of thallium to water via wastewater effluents, as determined from NPRI data (Section 5). These exposure scenarios include releases of thallium from: 1) metal mining activities, 2) base metal smelting and refining, and 3) coal-fired power generating facilities in Canada. While releases from wastewater treatment facilities (WWTFs) were considered, an exposure scenario was not quantitatively developed. Albeit not included in this screening assessment, exposure scenarios of thallium releases from other sectors (e.g., pulp and paper, oil sands, and landfills) were explored by ECCC, and available data did not show ecological risk for the releases of thallium into surface water from these sectors.

PECs were primarily estimated using measured concentrations of thallium in surface water as they provide evidence for thallium exposure to organisms resulting from specific sectors of activity in Canada. When both total and dissolved Tl concentrations were available, total Tl concentration was considered due to the ready water solubility and very weak complexation tendency of Tl(I) with ligands in the aquatic environment in the environmental exposure analysis. The adequacy of measured environmental concentrations was assessed considering various factors such as the year and the season of the sample collections, analytical method used and its detection limits, and number of available measurements. Although based on measured concentrations,

PECs are labelled as "predicted" because measurements taken from specific sites for a sector of activity are used to represent the sector as a whole.

When measured concentrations were unavailable, PECs were estimated using a default flow rate of thallium in effluent. Given that organisms in aquatic ecosystems are exposed to both natural and anthropogenic sources of thallium, background concentrations were also considered to estimate their total exposure. Therefore, for a particular site, PECs were calculated by adding the appropriate median background concentration of total thallium in surface water (Table 7-3) to the estimated aquatic concentrations (EAC) of thallium in the receiving environment resulting from the specific activity (i.e., PEC = EAC + median background concentration). When relying on yearly average loadings of thallium in effluent, EACs were determined by applying a dilution factor of 10 to measured effluent concentrations.

7.2.3 Metal mining

Thallium is a low-level-constituent of many ores; it also co-exists with sulfide ores of lead, zinc, copper and iron, or with the minerals associated with cadmium, iron, and potassium, albeit primarily of copper, zinc and lead mined in Canada (Section 4.2.1). For the years 2014-2017, total yearly release of thallium and its compounds to water reported to the NPRI by the metal mining sector ranged from 31 to 55 kg (Section 5 of this report) (NPRI 2018).

Canadian metal mines that release effluents at any time into any water at a flow rate exceeding 50 m^3/day are subject to the *Metal and Diamond Mining Effluent Regulations* (MDMER 2018) under the *Fisheries Act*. Thallium was not required to be reported as part of the effluent characterization under pre-2018 MDMER, but 39 metal mining facilities voluntarily reported thallium effluent releases in the environment during 2013-2017 as part of the Environmental Effects Monitoring (EEM) program (EEM 2018). Thallium has been added to Schedule 5 to be monitored as part of the EEM program under the amended MDMER (Canada 2017b). For thallium determination in water and effluents under the MDMER, an analytical method detection limit (MDL) of 0.4 µg/L is in effect (Canada 2017b).

Concentrations of Tl measured in 2013-2017 in surface water samples collected from exposure areas and reference areas, and submitted to ECCC through the MDMER reporting system as part of the EEM program (EEM 2018) were used for the data analysis. According to the MDMER, the exposure area refers to fish habitat and waters frequented by fish that are exposed to metal mining effluent, whereas the reference area refers to waters frequented by fish that are not exposed to metal mining effluent and have similar fish habitat to that of the exposure area (see Schedule 5 of the MDMER).

Site-specific calculations for thallium concentrations were performed for ten mining facilities (including one facility with combined effluents from a metal mine and a base metal smelter). Submitted Tl data (for the 5-year reporting period) indicate that at

exposure sites, Tl detection frequency was 10% higher compared to the reference sites (Figure 7-2). The MDLs ranged from 0.002 to 10 µg Tl/L. Samples from the facilities with MDL greater than the PNEC$_{water}$ value and contained more than 1/3 of non-detectable samples in the dataset are excluded from analysis due to considerable uncertainty (false positive). The percentage of analytically detectable concentrations in the exposed and reference areas for each facility during the 5-year reporting period ranged within 17% - 100% and 0% - 72%, respectively. Analytically non-detectable concentrations were substituted with the ½ MDL, while the blank samples and samples with the values of 0 µg Tl/L (without reported MDLs) were removed from the data analysis.

Box plots of Tl concentrations for the exposure and reference areas of ten facilities are presented in the form of thallium surface water concentrations (Figure 7-2). The red line represents PNEC$_{water}$ of 0.8 µg/L relative to thallium concentrations measured. These ten facilities were selected from the 39 facilities based on the order of magnitude of thallium elevation in the exposure area(s) and sample size (i.e., more than two years of data per facility since sampling is conducted quarterly).
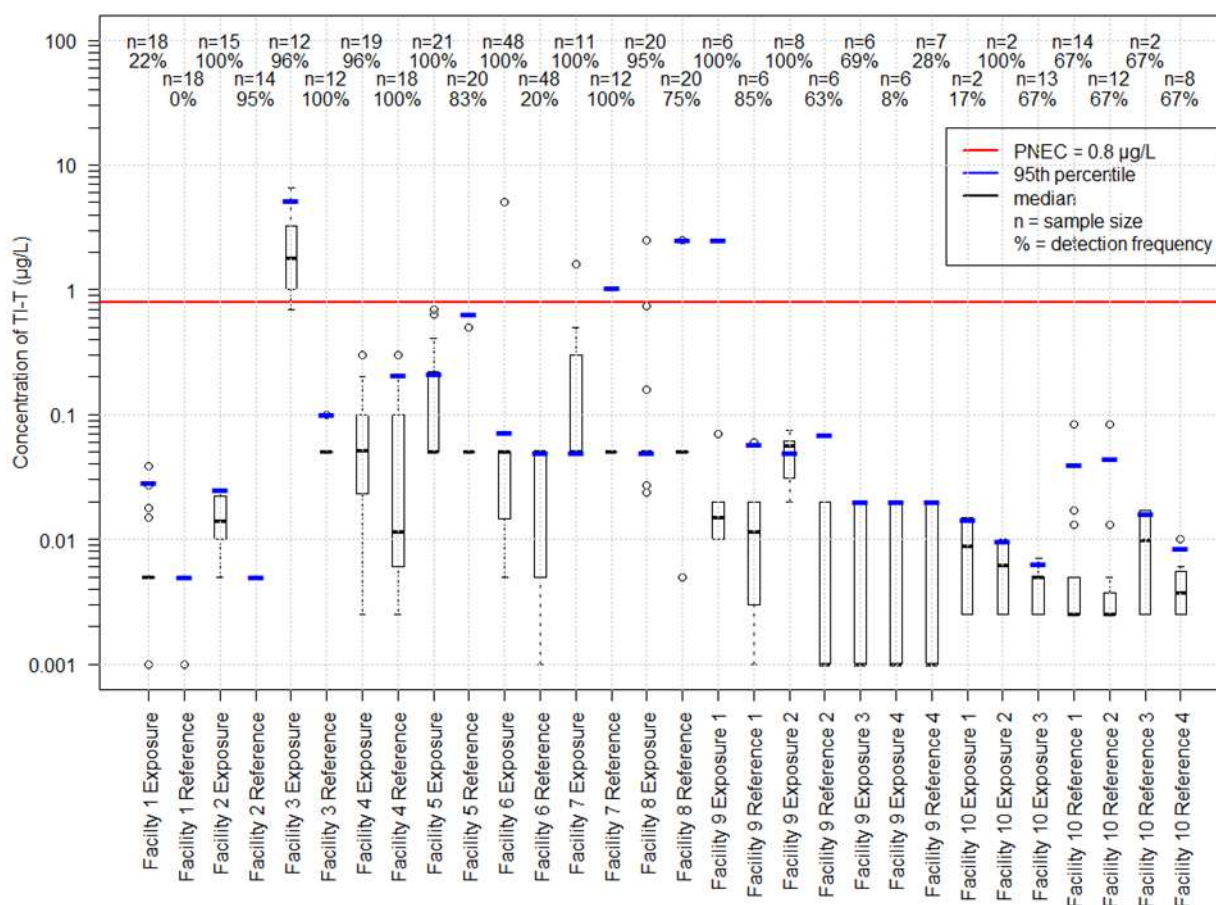
Figure 7-2. Box plots for thallium in surface water reported under the MDMER for ten metal mining facilities (2013 - 2017)

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Elevated thallium concentrations in surface water samples from the exposure areas of three mining facilities indicate that Tl is released into the aquatic environment by this industrial sector. Median thallium concentrations in exposed areas of the three metal mining facilities (Facility 1, 2, and 9) were 2 to 5 times higher than median concentrations from the reference areas. However, the geometric mean, median, and 95th percentile Tl concentrations were all below PNEC$_{water}$ of 0.8 µg/L, indicating low to moderate Tl increase from metal mining effluents at a relatively small number of facilities. Facility 3 had significantly (36-fold) higher measured Tl concentrations at the exposure area with the median Tl concentration of 1.8 µg/L and exceeded the PNEC$_{water}$ (0.8 µg/L) in 75% of the measurements during 2014 – 2016.

It should be noted that less than 30% of metal mining facilities reported Tl measurements during 2013-2017. Further data analysis of Tl releases by the sector could be conducted more comprehensively including all facilities when Tl will be subjected to formal reporting under the MDMER and EEM (i.e., post-2018).

7.2.4 Base metal smelting and refining (BMS)

There are currently eleven major base metals smelting and refining (BMS) facilities in Canada located in Alberta, British Columbia, Quebec, Manitoba, New Brunswick, Newfoundland & Labrador, and Ontario. The BMS sector processes concentrates from metal mines and mills as well as recycled materials (e.g., electroplating, batteries) to purify, produce and recover metals. Thallium is one of the residues or by-products produced during smelting processes. In 2014 – 2017, releases of thallium and its compounds to water reported to the NPRI by BMS facilities ranged within 1 441 – 3 067 kg, with releases increasing each year during 2014 – 2016, and decreased in 2017 (Section 5 of this report; NPRI 2018). Annual releases to land reported to the NPRI by the sector in the same period of 2014 – 2017 were negligible (NPRI 2018).

Releases from primary and secondary copper smelters and copper refineries, and releases from primary and secondary zinc smelters and zinc refineries were assessed under the Priority Substances List (PSL) approach (Canada 2001). Air emissions from these facilities were concluded to be toxic under CEPA (Canada 2001) and particulate matter containing metals released in emissions from copper and zinc smelters of refineries were listed on Schedule 1 of CEPA in 2003. Base metal smelting and refining facilities in Canada were subsequently subject to air emissions requirements set under the Pollution Prevention Planning notice published in the *Canada Gazette* in 2006 (Canada 2006). The Notice includes release limits for particulate matter, which contain most of the metals emitted to air, including thallium. Therefore, this assessment focuses on releases of thallium to the aquatic environment as a result of effluent discharges, and air emissions from BMS facilities are not explicitly considered.

Five BMS facilities have combined effluents with metal mines and one of these facilities voluntarily submitted measured Tl concentrations from 2014 to 2017 as a part of the EEM program under the MDMER (EEM 2018). Thallium concentrations measured in

surface water in the two exposure areas downstream of the effluent discharge and in the two reference areas for Facility 1 are summarized in Table 7-4. Measured Tl concentrations in both exposure and corresponding reference sites were at the same level and were below the PNEC$_{water}$, suggesting no significant increase of Tl in the receiving environment from the effluent releases from this facility.

Table 7-4. Site-specific Tl concentrations in surface waters reported in 2014 – 2017 by base metal smelters and refineries under the MDMER

Facility (Code)	Type of area	Sample size (detectable)	Tl conc. > PNEC (%)	Geometric mean [c] (µg/L)	Median [c] (µg/L)	95th percentile [c] (µg/L)
1	Exposure [a]	16 (0)	0%	0.032	0.05	0.05
1	Reference [b]	16 (2)	0%	0.039	0.05	0.05
1	Exposure [a]	16 (0)	0%	0.032	0.05	0.05
1	Reference [b]	16 (0)	0%	0.032	0.05	0.05

[a] Exposure area refers to all fish habitat and waters frequented by fish that are exposed to effluent (Schedule 5 of the MDMER).
[b] Reference area refers to water frequented by fish that is not exposed to effluent and that has fish habitat that, as far as practicable, is most similar to that of the exposure area (Schedule 5 of the MDMER).
[c] Detection limit at 0.1 – 0.01 µg/L.

Earlier EEM reports were also reviewed and information on Tl concentrations was analyzed for some additional facilities which did not submit data through the MDMER reporting tool (EEM 2018). Measured Tl concentrations in surface water were available for three additional BMS facilities with effluents combined to that of a metal mine (for varying reporting years). Measured Tl concentrations at the exposure and reference sites are summarized as ranges instead of geometric means, median concentrations, or 95th percentile due to inconsistency in reported sample sizes and the selection of exposure sites (Table 7-5). All Tl measurements in exposure and reference sites were within the same range, which suggests low increase of Tl from the effluent releases from these facilities. Importantly, all measured Tl concentrations were below the PNEC$_{water}$ of 0.8 µg/L.

Table 7-5. Site-specific Tl concentrations in surface waters reported from 2004 to 2014 by base metal smelters and refineries under the MDMER

Facility (Code)	Reporting Year	Type of area	Sample size (detect)	Detects > PNEC (%)	Range of Tl concentration (µg/L)
4	2008-2010	Exposure [a]	6 (0)	0%	< DL (0.1 – 0.3)
4	2008-2010	Reference [b]	11 (0)	0%	< DL (0.1 – 0.3)
5	2004-2014	Exposure [a]	77 (54)	0%	< DL (0.002 – 0.1) – 0.2
5	2004-2014	reference [b]	33 (12)	0%	< DL (0.002 – 0.1) – 0.1
6	2006-2011	Exposure [a]	6 (5)	0%	0.0025 – 0.026
6	2006-2011	Reference [b]	1 (0)	0%	< DL (0.01)

Abbreviation: DL = detection limit at 0.002 - 0.3 µg/L.

Tl environmental releases from two stand-alone facilities (Facilities 2 and 3) that are not subject to the MDMER were also considered. Thallium concentrations for Facility 2 were available in receiving waters (exposed areas) and reference areas from a period of 2011 to 2013 (Table 7-6) (Ecoscape Environmental consultants Ltd. and Larratt Aquatic Consulting Ltd. 2014). A total of 120 (58% detects at MDL of 0.002 µg/L) and 197 (91% detects at MDL of 0.002 µg/L) surface water samples were collected from two references and six exposure sites, respectively, during July 2011 to April 2013. Transect surface water samples were collected 3-35 m downstream of the three effluent discharge sites (Discharge site II, III, IV) during low flow seasons in 2011. Two of the three thallium samples collected in July 2011 from the Discharge site III were above the PNEC$_{water}$ (i.e., 0.98 and 1.16 µg/L). Thallium concentrations were reduced to below 0.02 µg/L at the same location in November 2011, suggesting that Tl releases at the site are likely of concern during low flow seasons. Thallium concentrations from Discharge site II and IV were all below the PNEC$_{water}$ during the same sampling periods. Regular surface water samples were collected from two reference sites and three exposure sites (Table 7-6). Exposure area 2 is the initial dilution zone located 0.23 km downstream of the effluent Discharge site II. Samples collected at that location showed relatively high Tl concentrations at the geometric mean and 95th percentile and 2 measurements (3%) were above the PNEC$_{water}$; however, the median concentrations of Tl are in the same range as those from the reference areas (Table 7-6). Thallium median and/or geometric mean concentrations in surface water in three exposure areas (exposure 2, 3, 4) and discharging sites II and III are greater than the corresponding concentrations relative to the reference areas, confirming the release of Tl into the aquatic environment by the facility.

Table 7-6. Concentrations of total Tl in reference areas and receiving environment from Smelter Facility 2 during 2011 – 2013 (Ecoscape Environmental consultants Ltd. and Larratt Aquatic Consulting Ltd. 2014)

Type of area	Sample size (detect)	Detects > PNEC (%)	Concentration range (µg/L) [g]	Geometric mean (µg/L)	Median (µg/L)	95th Percentile (µg/L)
Discharge site II [a]	6 (6)	0%	0.0277 – 0.4	0.09	0.13	0.36
Discharge site III [a]	6 (6)	33%	0.0073 – 1.16	0.10	0.32	1.12
Discharge site IV [a]	6 (4)	0%	< DL – 0.0023	0.0019	0.0024	0.0032
Exposure 2 [b]	59 (50)	3%	< DL – 1.06	0.0105	0.0029	0.78
Exposure 3 [c]	59 (53)	0%	< DL – 0.134	0.0116	0.0166	0.123
Exposure 4 [d]	61 (61)	0%	0.0034 – 0.107	0.0129	0.0114	0.0294
Reference 1 [e]	59 (32)	0%	< DL – 0.0044	0.0017	0.0021	0.0036
Reference 2 [f]	61 (38)	0%	< DL – 0.0039	0.0018	0.0021	0.0035

[a] Discharge sites II, III, IV are the area located 5-35 m downstream of the CII, CIII, CIV outfalls.
[b] Exposure 2 is the initial dilution zone located 0.23 km downstream of the CII outfall, ~0.72 km downstream of CIII outfall.
[c] Exposure 3 is the area located 1.09 km downstream of the CII outfall.
[d] Exposure 4 is the area located 15.8 km downstream of the CII outfall.
[e] Reference 1 is the area located 1.975 km upstream of the CII outfall.
[f] Reference 2 is the area located 9.72 km upstream of the CII outfall.
[g] DL = Detection limit at 0.002 µg/L.

As identified in the transect surface water samples for Facility 2, two of the six samples collected at Discharge site III exceeded PNEC$_{water}$ in 2011, suggesting potential concern for Tl elevation in the vicinity of the site. No other measurements were reported at the site in the facility's environmental report (Ecoscape Environmental consultants Ltd. and Larratt Aquatic Consulting Ltd. 2014). Therefore, as a further line of evidence, the predicted Tl environmental concentration was also estimated from the annual aquatic releases reported to the NPRI by the facility during 2014-2017. The average annual Tl releases to water and a dilution factor of 10 were used in calculating the thallium estimated aquatic concentrations (EAC) as described in Section 7.2.2. The PEC for the receiving water was calculated as the sum of EAC and the median background concentrations for the ecozone where the facility was located. The calculated PEC was 1.13 µg/L, which is 1.4 times higher than the PNEC$_{water}$, indicating concern for Tl release by the facility.

For Facility 3, the thallium PEC was estimated from the annual aquatic releases reported to the NPRI by the facility during 2014-2017. The calculated PEC was 2.72

µg/L, which is 3.4 times higher than the PNEC$_{water}$ of 0.8 µg/L, indicating very high likelihood of environmental impact from Tl release by the facility.

7.2.5 Coal-fired electric power generation plants

The volatilization of thallium from coal burning at high temperatures and subsequent re-condensation on finer ash particles result in up to 10 times higher thallium concentrations on ash particles than in the coal itself (Cheam 2001). Deposition of fly ashes and effluent released from ash lagoons from the power generation sector has the potential to release Tl into the environment. Limited data are available for thallium concentrations near these facilities. Annual releases of 30 – 62 kg of thallium to air from this sector in Canada were reported during 2014 – 2017. No Tl release to water from coal-fired power stations was reported during the same period (NPRI 2018).

In 2006, the CCME endorsed the implementation of Canada-wide Standards (CWS) for Mercury Emissions from Coal-fired Power Stations (CCME 2006). Although the purpose of the standards was to reduce mercury emission from flue dusts, technology developed also reduced overall particulate emissions to air, including co-existing heavy metal elements such as thallium.

In 2005, after the Lake Wabamun oil spill, the Alberta Ministry of the Environment conducted water quality surveys of Wabamun Lake where two coal-fired power plants are located (Alberta Environment 2006). The thallium concentration measured in 54 water samples collected in the pelagic zone of the lake were all below the MDL of 0.003 µg/L (Alberta Environment 2006). In comparison, 33 samples collected in 2002 in that lake, had a maximum thallium concentration of 0.011 µg/L (with a MDL of 0.005 µg/L). Therefore, the PEC for Lake Wabamun is based on the data from 2002 (Table 7-7).

Table 7-7 summarizes measured thallium concentrations in effluents and receiving surface waters in the vicinity of seven power generation facilities across Canada by Cheam (2000, 2001). Facilities that are now closed have been excluded from the data collection. Discharges from ash lagoons, leachate ponds, and wastewaters were considered as effluents, and a dilution factor of 10 is applied to the concentrations of Tl in these effluents to calculate respective thallium EAC. The PEC was calculated as previously described. The calculated PECs in downstream discharges from an ash lagoon were found to exceed PNEC$_{water}$ at one facility.

Table 7-7. Concentrations of Tl in environmental water samples in the vicinity of power generation facilities across Canada by 2000

Facility (code)	Location	Tl concentration [c] (µg/L)	EAC [c] (µg/L)	PEC [c,d] (µg/L)
1	Creek below the facility Reservoir [a]	0.10	0.10	0.10
2	Discharge site [b]	0.06	0.01	0.06

Facility (code)	Location	Tl concentration [c] (µg/L)	EAC [c] (µg/L)	PEC [c,d] (µg/L)
3	2 km east from the facility [a]	0.29	0.29	0.29
3	Treated discharge [b]	4.0	0.40	0.45
3	Ash leachate pond discharge [b]	5.1	0.51	0.56
4	Waste water discharge to lagoon [b]	0.89	0.09	0.14
5	Ash leachate pond discharge [b]	0.40	0.04	0.09
5	Waste water discharge [b]	0.56	0.06	0.11
6	Final wastewater discharge – treated [b]	0.37	0.04	0.09
6	Ash leachate pond discharge [b]	1.0	0.10	0.15
7	Ash lagoon discharge [b]	24	2.4	2.9
7	Pit B discharge [b]	0.98	0.10	0.15
8 & 9	Lake Wabamun [a]	0.01	0.01	0.01

Abbreviations: EAC, Estimated Aquatic Concentrations; PEC, Predicted Environmental Concentrations
[a] The sites are considered as measured Tl concentration in the receiving water environment, no dilution factor or background concentrations are applied.
[b] Considered as effluent concentration, apply dilution factor of 10 to calculate EAC.
[c] All values rounded up to 2 significant figures.
[d] PEC = EAC + median background concentration based on ecozones where the facilities are located (Table 7-3).

7.2.6 Wastewater treatment plants

Thallium may be released to wastewater from the use of pharmaceuticals, manufacturing of dyes and fireworks, and chemical reactions that contain thallium (Couture et al. 2011) and end up at wastewater treatment facilities. A Canadian wastewater treatment plant estimated releasing approximately 300 kg of thallium to water during 2014 – 2015 (NPRI 2017). Since most of the samples (94% in 2014 and 100% in 2015) had Tl concentrations that were below the MDLs, the estimates were derived as ½ MDLs; these values can be considered as over-estimates. In 2016 and 2017, this plant removed thallium from their list of reportable substances, as there were "no results above the method detection limit (MDL) in two years" (NPRI 2017).

During 2009 – 2012, thallium releases were monitored at 25 wastewater treatment plants across Canada under the CMP wastewater research and monitoring project (Environment Canada 2013a). Final effluent samples were analyzed for the total thallium concentrations in water. Thallium was quantitatively detected only in one (1) out of 191 (i.e., 0.5 %) final effluent samples with the concentration being 0.059 µg/L.

Therefore, it is assumed that thallium is rarely present in wastewater final effluents, at a concentration above a MDL of 0.01 µg/L.

Although no direct releases to soil are anticipated, indirect releases may result from the application of Tl-containing biosolids (from wastewater treatment systems) on agricultural lands. In Canada, thallium is not regulated in biosolids, albeit its levels have declined significantly in recent decades with reported median Tl concentration in biosolids of 0.26 mg/kg (WEAO 2010). Similar low levels (in ~10% samples) or quantitatively non-detectable levels were reported from 25 wastewater treatment plants across Canada during 2009 – 2012 (ECCC 2016). A total of 112 primary sludge samples, 78 waste biological sludge samples, and 135 treated biosolids samples were analyzed for total thallium. Thallium was detected above the MDL of 0.001 mg/kg in 37 of the 325 solids samples (i.e., in 11% of samples), with maximal concentrations of 0.0168, 0.134, and 0.814 mg/kg in primary sludge, waste biological sludge, and treated biosolid samples respectively.

Hebert et al. (2011) studied impact of biosolids application on Tl concentrations in dairy milks at Saguenay farms of Quebec (Canada), where biosolids have been applied to the soils for multiple years. Thallium was not detected above detection limit in either biosolids (0.1 mg/kg) or cow milk (0.01 mg/L).

Data from the CMP monitoring project and the NPRI suggest that annual thallium releases to water or input from biosolids on agricultural lands from wastewater treatment plants are insignificant. Therefore, the pathway of thallium exposure via the wastewater sector is not pursued further.

7.3 Characterization of ecological risk

The approach taken in this ecological screening assessment was to examine assessment information and develop proposed conclusions using a weight of evidence approach and using precaution as required under CEPA. Evidence was gathered to determine the potential for thallium and its compounds to cause harm in the Canadian environment. Lines of evidence considered include those that directly support the characterization of ecological risk (e.g., measured endpoints or properties), and indirect lines of evidence (e.g., classification of hazard or fate characteristics by other regulatory agencies).

7.3.1 Risk quotient analysis

Risk quotient (RQ) analyses were performed by comparing estimates of exposure (PECs; see the Ecological Exposure Assessment section 7.2 of this report) with ecological toxicity information (PNECs; see the Ecological Effects Assessment section 7.1) to determine whether there is potential for ecological harm in Canada. Specifically, RQs were calculated for the aquatic compartment (i.e., surface freshwaters or marine waters) in the exposure scenarios described in Section 7.2 for three sectors: metal mining, base metals smelting, and coal-fired power generation stations.

The metal mining sector ecological risk characterization utilized raw surface freshwater data submitted to the EEM program under the MDMER for the period of 2013 to 2017 (EEM 2018). Therefore, the PECs consisted of measured Tl concentrations in the receiving environments (i.e., exposure areas) and corresponding reference areas of metal mining facilities. For ecological risk characterization, RQs were calculated for ten metal mining facilities identified for ecological exposure assessment in Section 7.2.3 of this report. Boxplots (Figure 7-2) generated for the ten facilities displayed the distribution of RQs, with a red line to indicate where the RQ is equal to one (threshold for the risk). The results of the RQ calculations show that one facility demonstrates potential for ecological risk (RQ of up to 2.25) due to effluent releases of Tl.

The base metals smelting sector ecological risk characterization utilized raw surface fresh and marine water data, including EEM program data for the four facilities which combine their effluents with metal mines for periods up to 2017 (EEM 2018), data reported to NPRI for two stand-alone facilities (NPRI 2018), and data from an environmental assessment report for one of these facilities (Ecoscape Environmental Consultants Ltd. and Larratt Aquatic Consulting Ltd. 2014). Table 7-8 presents the RQs calculated for all six BMS facilities. Data demonstrate that Facility 3 showed clear evidence of ecological risk (RQ of up to 3.4) due to releases of effluent containing Tl. Facility 2 showed potential of ecological risk (RQ of up to 1.4) due to releases of Tl at one of its discharge points during low flow season.

Table 7-8. Summary of risk quotients obtained exposure scenarios for BMS facilities releasing effluents to water

Facility code	PECs	PNEC$_{water}$	RQs
1	0.05 µg/L [a]	0.8 µg/L	0.06
2	< DL to 1.13 µg/L [b]	0.8 µg/L	up to 1.4
3	2.72 µg/L [c]	0.8 µg/L	3.4
4	< DL (0.1 – 0.3) µg/L [d]	0.8 µg/L	< 0.38
5	< DL to 0.2 µg/L [d]	0.8 µg/L	up to 0.25
6	0.0025 to 0.026 µg/L [d]	0.8 µg/L	0.003 to 0.032

Abbreviations: DL, Detection Limit; PEC, Predicted Environmental concentration; PNEC, Predicted No-Effect Concentration; RQ, Risk Quotient

[a] PECs are presented as thallium median concentrations as calculated in Section 7.2.4.
[b] PECs are presented as thallium concentrations as a range of measured and modelled in Section 7.2.4.
[c] PECs are presented as thallium concentrations modelled in Section 7.2.4.
[d] PECs are presented as a range of measured thallium concentrations in Section 7.2.4.

The ecological risk characterization for the coal-fired power-generating sector utilized raw freshwater data published by Cheam (2001) and the results of the water quality surveys of Wabamun Lake (Alberta Environment 2006). The PECs include measured data for Tl from downstream surface freshwater of the discharge sites of the power-generating plants, or were calculated by applying a dilution factor of 10 to the concentrations of Tl in the effluents of wastewater discharge lagoons. One facility showed potential of ecological risk due to releases of Tl at the discharge point of its ash lagoon, with estimated RQ of 3.6 (PEC of 2.9 µg/L). The available exposure data

suggest that the remaining coal-fired power generating facilities did not pose ecological risk from effluents discharged to the surface freshwater.

Table 7-9 summarizes the calculated RQs for industrial exposure scenarios for thallium discussed in the screening assessment.

Table 7-9. Risk quotient calculations for industrial exposure scenarios for thallium

Exposure scenario	Medium	PEC range	PNECs	RQ range	No. of facilities with RQ > 1
Metal mining	Water	0.001 to 1.8 µg/L [a]	0.8 µg/L	0.001 to 2.25	1[b] (in 39)
Base metal smelting and refining (4 BMS facilities with combined metal mining effluents, and 2 stand-alone facilities)	Water	0.0025 to 2.72 µg/L [b,c]	0.8 µg/L	0.003 to 3.4	2 (in 5)
Coal-fired electric power generation	Water	0.056 to 2.9 µg/L [d]	0.8 µg/L	0.07 to 3.6	1 (in 9)

Abbreviations: PEC, Predicted Environmental Concentration; PNEC, Predicted No-Effect Concentration; RQ, Risk Quotient.
[a] PECs are presented as thallium median concentrations as calculated in Section 7.2.4.
[b] PECs are presented as thallium concentrations as a range of measured and modelled in Section 7.2.4.
[c] PECs are presented as thallium concentrations modelled in Section 7.2.4.
[d] PECs are presented as a range of measured thallium concentrations in Section 7.2.4.

7.3.2 Consideration of the lines of evidence

To characterize the ecological risk of thallium and its compounds, technical information for various lines of evidence was considered (as discussed in the relevant sections of this report) and qualitatively weighted. The key lines of evidence supporting the assessment conclusion are presented in Table 7-10, with an overall discussion of the weight of evidence provided in section 7.3.3. The level of confidence refers to the combined influence of data quality and variability, data gaps, causality, plausibility and any extrapolation required within the line of evidence. The relevance refers to the impact the line of evidence has when determining the potential to cause harm in the Canadian environment. Qualifiers used in the analysis ranged from low to high, with the assigned weight having five possible outcomes.

Table 7-10. Weighted lines of key evidence considered to determine the potential for thallium and its compounds to cause harm in the Canadian environment

Line of evidence	Level of confidence [a]	Relevance in assessment [b]	Weight assigned [c]
Persistence in the environment	High	Moderate	Moderate – high
Bioaccumulation in aquatic and/or terrestrial organisms	Low	Moderate	Low – moderate
Long-range transfer potential	Moderate	Low	Low – moderate
PNEC for aquatic organisms in water	High	High	Moderate – high
PNEC for organisms in soil	Moderate	Moderate	Moderate
Monitoring data for concentrations of thallium in surface freshwater (PECs for metal mining)	High	High	High
Monitoring data for concentrations of thallium in surface freshwater (PECs for base metal smelting)	Moderate	High	Moderate – high
Modelled data for concentrations of thallium in surface freshwater and marine water (PECs for base metal smelting)	Moderate	High	Moderate – high
Monitoring data for concentrations of thallium in surface freshwater (PECs for coal-fired power generation plants)	Low	Moderate	Low – moderate
RQ(s)	High	High	High

Abbreviations: PEC, Predicted Environmental Concentration; PNEC, Predicted No-Effect Concentration; RQ, Risk Quotient.

[a] Level of confidence is determined according to data quality, data variability, data gaps and if the data are fit for purpose.

[b] Relevance refers to the impact of the evidence in the assessment.

[c] Weight is assigned to each line of evidence according to the combined level of confidence and relevance in the assessment.

7.3.3 Weight of evidence for determining potential to cause harm to the Canadian environment

Once released into the environment, thallium and its compounds will dissolve/dissociate to release free thallium ions, resulting in potential exposure to aquatic and terrestrial organisms. Thallium is persistent and may have the potential for long-range transport to remote areas, thus remaining in the environment and resulting in long-term exposure to organisms. Thallium is not known to be an essential element for living organisms.

Thallium (Tl(I) in particular) is taken up by and bioaccumulates in both aquatic and terrestrial organisms. Considerably elevated thallium concentrations in organisms near sources of release (e.g., smelters) have been reported. However, no conclusion could be reached pertaining to thallium's biomagnification potential in ecosystems due to conflicting information.

Thallium has two oxidation states, Tl(I) and Tl(III), and its speciation in surface waters depends on the physical-chemical properties of the given waterbody. Thallium(I) is the more thermodynamically stable form under neutral environmental conditions. Thallium(III) is the primary form reported in the Great Lakes, likely existing in inert hydroxide form, and may ultimately precipitate to sediments from the water column. Bioavailability, uptake, and bioaccumulation of thallium in organisms is, however, dependent upon Tl activity and Tl(I) is the more relevant ecotoxicological species. Competitive interference with vital potassium-dependent biological processes in living organisms is a well-known mechanism of thallium toxicity. Potassium is identified as a potential toxicity modifying factor for reducing thallium toxicity in aquatic organisms; however, there is currently insufficient data for it to be considered as a toxicity modifying factor in the derivation of the PNEC$_{water}$.

Thallium is released to the aquatic compartment from many industries, including metal mining, base metal smelting, and coal-fired power generation stations. For most facilities, releases are limited and are unlikely to pose ecological risk, but a small number of facilities may release thallium to an extent that causes ecological risk. As discussed in Section 7.3.1, there is the potential for ecological risk caused by Tl in the aquatic environment due to effluent releases and ash lagoon discharges from base metal smelting and coal-fired power generation stations. Two of the six BMS facilities release effluents containing thallium that result in environmental concentrations higher than the PNEC$_{water}$, with maximum risk quotients of ~ 1.4 to 3.4. One (out of nine) coal-fired power generation facilities was releasing thallium into water that resulted in concentrations higher than the PNEC$_{water}$, with a maximum risk quotient greater than 3.

In the metal mining sector, the exposure to thallium is generally not of concern with current exposure data available (Facility 3 discussed in Section 7.2.3); however, approximately only one third of metal mining facilities in Canada reported environmental concentrations of thallium under MDMER/EEM in the past 5 years. Thallium has been added to the amended MDMER/EEM reporting requirement with a new MDL of 0.4 μg/L, beginning in 2018, which could inform further analysis.

Thallium uses (Section 4.3) and NPRI data (Section 5) suggest that wastewater treatment plants may release thallium to the environment. However, further data submitted to NPRI and information from ECCC's CMP research and monitoring projects indicate that thallium releases from these facilities are of low concern.

This information indicates that thallium and its compounds have the potential to cause ecological harm in Canada.

7.3.4 Sensitivity of conclusion to key uncertainties

Exposure and risk characterization scenarios for thallium in surface water were developed for three sectors: metal mining, base metals smelting and refining, and coal-fired electric power generation stations.

In the metal mining sector in Canada, information on thallium concentrations in receiving surface waters or in effluents is limited as data are only available for approximately one third of the facilities. In the near future, once extensive high quality environmental monitoring data for thallium are available for the sector, further data analysis can be performed for better understanding of the potential impacts of this industrial sector. Similarly, the risk characterization focusing on thallium in the base metals smelting sector was limited to six of eleven facilities, where exposure data were available for surface water. The exposure data in ash lagoons for coal-fired power generation plants were dated pre-2006, so may not reflect current exposure levels. A higher percentage of particulates (including thallium) recovered from flue dusts ending up in ash lagoons may ultimately result in lower thallium concentrations discharged into surface water with the implementation of Canada-wide Standards for Mercury Emissions from Coal-fired Power Stations (CCME 2006).

The PECs for the two stand-alone base metals smelting facilities and the coal-fired power generation exposure scenario were estimated from effluent concentrations. Site-specific data could avoid the need to incorporate a dilution factor, or a representative background concentration.

Some datasets of measured environmental concentrations contained non-detects and these were replaced with half the reported detection limit (DL). A sensitivity analysis was conducted to determine if the replacement choice (1/2DL) produced false positives in the ecological risk outcome. However, replacement with 0 and with 1/2DL yielded similar results.

Exposure and reference areas may be located downstream and upstream on the same waterbody, or may be located on different waterbodies (i.e., not necessarily upstream and downstream paired). It appears that in some cases the thallium concentration in the reference area may be influenced by natural or anthropogenic factors that lead to higher values than in the designated exposure area. While potentially observed for some facilities, this confounding factor, however, was not important enough to influence the weight of evidence in the risk characterization.

Total Tl concentrations were preferred over dissolved Tl concentrations when both sets of data were available in the environmental exposure analysis. While potentially conservative, it was recognized that Tl(I) is the primary species of concern in receiving water environment through anthropogenic releases. Due to the ready solubility and very weak complexation tendency of Tl(I) with ligands in surface water, total Tl concentrations measured were often in close proximity (~80%) to dissolved Tl concentrations when both sets of data were available.

Incorporating toxicity modifying factor(s) in the derivation of PNECs may provide environmentally realistic site-specific analysis for thallium exposures. In the current assessment, the PNEC$_{water}$ does not consider TMF due to insufficient data, although there is some evidence that potassium may potentially reduce thallium toxicity to certain aquatic organisms. It is recognized that a derived PNEC value that does not consider TMF may, in some cases, be conservative, and therefore more protective of aquatic organisms over the long-term.

No conclusion can be reached on the potential of thallium biomagnification in both aquatic and terrestrial food chains due to contradictory data. However, thallium is easily assimilated by various organisms and therefore has the potential to accumulate as evidenced by elevated thallium concentrations in organisms near sources of releases. It is recognised that current understanding of thallium bioaccumulation and consequential effects in environmental receptors is limited, thus requires further collection of data to quantify the critical tissue level concentrations of thallium and subcellular effects over chronic exposure, as well as the thallium detoxification mechanisms and routes by various organisms.

8. Potential to cause harm to human health

Thallium is a naturally occurring element that is present in environmental media in Canada. Total thallium concentration has been measured in drinking water distribution systems, household dust, and indoor and outdoor air (NAPS 2011; Health Canada 2016; Rasmussen et al. 2016; Tugulea et al. 2016). Food is the primary source of thallium exposure for Canadians. Thallium was measured as part of the Total Diet Study from 1993 to 1999; average dietary intake for all age groups was 0.029 µg/kg bw/day (Health Canada [modified 2011]). Toddlers had the highest dietary intake at 0.088 µg/kg bw/day, and dietary intakes of thallium declined with age. Thallium is present in breast milk as a contaminant and is a source of exposure for nursing infants. Average and 95th percentile intakes of 0.0089 µg/kg bw/day and 0.011 µg/kg bw/day, respectively, were derived based on measured concentrations in breast milk from Canadian mothers (n=2001) between 2008 and 2011 as part of the core MIREC study (personal communication, 2016 email from the Bureau of Chemical Safety, Food Directorate, to the Existing Substances Risk Assessment Bureau, Health Canada, unreferenced, Arbuckle et al. 2013).

Neurological symptoms, including sleep disorders, tiredness, weakness, nervousness, headache, other psychiatric alterations, and neurological and muscular problems have been reported with chronic exposure to thallium in humans (IRIS 2009). Other thallium induced symptoms, such as hair loss, dermal or gastrointestinal disorders have also been reported with chronic exposure to elevated levels of thallium in occupational settings (German Federal Environment Agency 2011).

The human health risks of thallium and its compounds were characterized using a science approach based upon biomonitoring data, entitled Biomonitoring-based Approach 2 (Health Canada 2016). The approach utilizes population-level biomonitoring

data from large scale surveys, such as Canadian Health Measures Survey (CHMS) and the United States (U.S.) National Health and Nutrition Examination Survey (NHANES), as biomonitoring data provide valuable information on the prevalence and concentration of chemicals in the general population. The CHMS and the NHANES measure the concentrations of the substance or moiety in blood (whole blood, serum, plasma) and/or urine. Total concentrations of a substance in blood or urine may provide a biologically relevant, integrated measure of exposures that occur across multiple routes (e.g., oral, dermal and inhalation) and sources (including environmental media, diet, and frequent or daily use products to which people were exposed).

In the Biomonitoring-based Approach 2, biomonitoring data are compared with human biomonitoring guidance values, such as a biomonitoring equivalent (BE) or a German human biomonitoring value (e.g., HBM-I). BEs are typically derived from existing health-based exposure guidance values such as a reference dose (RfD) or a Tolerable Daily Intake (TDI). In general, exposure guidance values are converted to BEs using pharmacokinetic data or using regression correlations between external exposure and the biomarker concentrations (i.e., the chemical concentration in blood or urine). German HBM-I values are typically derived on the basis of human studies or epidemiology data. According to German Federal Environmental Agency, adverse health effects should not be expected when the chemical concentration of a body matrix (i.e., blood or urine) is below the HBM-I value (Angerer et al. 2011). A thorough review of available toxicokinetic data is an integral part of the Biomonitoring-based Approach 2. The approach is only recommended for use if the biomarker (i.e., chemical concentration in whole blood, plasma, serum or urine) is considered adequate to quantify exposure in the general population (Health Canada 2016). If exposures (on the basis of biomonitoring data) are below the human biomonitoring guidance value (i.e., BE or HBM-I value), then the substance or metal moiety is considered to be of low concern with respect to human health at current levels of exposure (Health Canada 2016).

The urine thallium concentrations in the general population of Canada and the USA were measured in the CHMS and the NHANES studies (Table 8) (Health Canada 2016).

The German human biomonitoring commission derived a HBM-I value of 5 µg/L or 6.4 µg/g creatinine (the creatinine conversion was based on the criteria presented in Hays et al. (2010), below which adverse health effects associated with thallium exposure in the general population are not expected (German Federal Environment Agency 2011; Health Canada 2016). The HBM-I value is based on data from two epidemiological studies in thallium-exposed workers and people living in the vicinity of an industrial source, which also formed the basis of the WHO-IPCS conclusion that 'renal thallium excreted rates less than 5 µg/L of urine have no detrimental health effects' (German Federal Environment Agency 2011). The median and the 95th percentile of urine concentrations from the biomonitoring data and the HMB-I value are presented in Table 8-1 below.

Table 8-1. Concentrations of total thallium in urine (µg/g creatinine) in the Canadian and United States population

Survey Population	Age Years	Median (95% CI)	95th Percentile (95% CI)	HBM-I	Exceedance
CHMS Cycle 2 [a] Canadian population (2009 to 2011)	3-79	0.21 (0.20 to 0.23)	0.55 (0.49 to 0.61)	6.4	N
NHANES [b] United States population (2013 to 2014)	6 and older	0.154 (0.139 to 0.163)	0.421 (0.414 to 0.438)	6.4	N

Abbreviations: CI=confidence interval, HBM-1 = human biomonitoring value level 1 (Germany), N=no
[a] Health Canada 2013
[b] CDC 2018

Data in table 8-1 demonstrates that total thallium urinary creatinine adjusted concentrations are more than an order of magnitude below the HBM-I value of 6.4 µg/g creatinine. Therefore, biomonitoring data from Canada and the U.S demonstrate that thallium-containing substances are of low concern at the current levels of exposure found in the general public. Further details are presented in the Biomonitoring-based Approach 2 science approach document (Health Canada 2016).

8.1 Uncertainties in evaluation of risk to human health

Uncertainties associated with the biomonitoring approach have been detailed in the science approach document (Health Canada 2016). Although there are no biomonitoring data for children under 3 years of age and children aged 1 to 4 years that have the highest dietary intakes (per body weight basis), there does not appear to be any age-related trends with thallium creatinine-adjusted urine concentrations. The hazard dataset for thallium is relatively robust, and it has been reviewed by international authorities. Uncertainty exists in the thallium health effects assessment, as the limited number of studies on the genotoxicity of thallium compounds provide inconsistent results regarding genotoxic potential, and the evidence for the carcinogenicity of thallium is inadequate for classification.

9. Conclusion

Considering all available lines of evidence presented in this draft screening assessment, there is risk of harm to the environment from thallium and its compounds. It is proposed to conclude that thallium and its compounds meet the criteria under paragraph 64(*a*) of CEPA as they are entering or may enter the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. However, it is proposed to conclude that thallium and its compounds do not meet the criteria under paragraph 64(*b*) of CEPA as

they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger to the environment on which life depends.

On the basis of the information presented in this draft screening assessment, it is proposed to conclude that thallium and its compounds do not meet the criteria under paragraph 64(*c*) of CEPA as they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health.

Therefore, it is proposed to conclude that thallium and its compounds meet one or more of the criteria set out in section 64 of CEPA.

It is also proposed that thallium and its compounds meet the persistence criteria as set out in the *Persistence and Bioaccumulation Regulations* of CEPA. It is considered that thallium and its compounds are easily assimilated by various organisms and have the potential to accumulate in both aquatic and terrestrial organisms. However, no conclusion can be reached on the potential of thallium biomagnification in both aquatic and terrestrial food chains considering the limited and contradictory data currently available.

References

Alberta Environment. 2006. <u>Wabamun Lake oil spill August 2005: data report for water and sediment quality in the pelagic area of the Lake (August 4-5 to September 15, 2005)</u>. [accessed 2019 Jan 31].

Al-Najar H, Schulz R, Römheld V. 2003. Plant availability of thallium in the rhizosphere of hyperaccumulator plants: a key factor for assessment of phytoextraction. Plant Soil. 249:97-105.

Anagboso MU, Turner A, Braungardt CB. 2013. Fractionation of thallium in the Tamar Estuary, south west England. J Geochem Explor. 125:1-7.

Angerer J, Aylward L, Hays S, Heinzow B, Wilhem M. 2011. Human biomonitoring assessment values: Approaches and data requirements. Int J Hyg Environ Health. 214(5):348-60.

Ankley GT, Di Toro DM, Hansen DJ, Berry WJ. 1996. Assessing the ecological risk of metals in sediments. Environ Toxicol Chem. 15:2053-2055.

Antisari LV, Marinari S, Ferronato C, Vianello G. 2016. Thallium-transfer from artificially contaminated soil to young Downy Oak plants (*QUERCUS PUBESCENS WILLD.*). Int J Environ Agric Res. 2(7):57-67.

Arbuckle TE, Fraser WD, Fisher M, Davis K, Liang CL, Lupien N, Bastien S, Velez MP, von Dadelszen P, Hemmings DG, et al. 2013. Cohort profile: the maternal-infant research on environmental chemicals research platform. Paediatr Perinat Epidemiol. 27(4):415-425.

[ATSDR] Agency for Toxic Substances and Disease Registry. 1992. Toxicological profile for Thallium. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA. p 129.

Babic M, Radic S, Cvjetko P, Roje V, Pevalek-Kozlina B, Pavlica M. 2009. Antioxidative response of *Lemna minor* plants exposed to thallium(I)-acetate. Aquat. Bot. 91:166-172.

Baceva K, Stafilov T, Matevski V. 2014. Bioaccumulation of heavy metals by endemic viola species from the soil in the vicinity of the As-Sb-Tl mine "allchar", Rebublic of Macedonia. Int J Phytoremediation. 16:347-365.

Baiocchi C, Giacosa D, Saini G, Cavalli P, Omenetto N, Passarella R, Polettini A, Trincherini PR. 1994. Determination of thallium in Antarctic snow by means of laser-induced atomic fluorescence and high-resolution Inductively-coupled plasma-mass spectrometry. Int J Environ Anal Chem. 55:211-218.

Benito V, Devesa V, Munoz O, Suner MA, Montoro R, Baos R, et al. 1999. Trace elements in blood collected from birds feeding in the area around Doñana National Park affected by the toxic spill from the Aznalcóllar mine. Sci Total Environ. 242:309-23.

Belowitz R, Leonard EM, O'Donnell MJ. 2014. Effects of exposure to high concentrations of waterborne Tl on K and Tl concentrations in *Chironomus riparius* larvae. Comp Biochem Physiol C. 166:59-64.

Belzile N, Chen YW. 2017. Thallium in the environment: A critical review focused on natural waters, soils, sediments and airborne particles. Appl Geochem. 84:218-243.

Bidoglio G, Gibson PN, O'Gorman M, Roberts KJ. 1993. X-ray absorption spectroscopy investigation of surface redox transformations of thallium and chromium on colloidal mineral oxides. Geochim Cosmochim Acta. 57(10):2389-2394.

Blumenthal B, Sellers L, Koval M. 2013. Thallium and Thallium Compounds. Kirk-othmer Encyclopedia of Chemical Technology. Wiley Online Library [accessed 2018 Sept 26]. [restricted access].

Borgmann U, Cheam V, Norwood WP, Lechner J. 1998. Toxicity and bioaccumulation of thallium in *Hyalella azteca,* with comparison to other metals and prediction of environmental impact. Environ Poll 99:105-114.

Borgmann U, Norwood WP, Dixon DG. 2004. Re-evaluation of metal bioaccumulation and chronic toxicity in *Hyalella azteca* using saturation curves and the biotic ligand model. Environ Pollut. 131:469-484.

Boughriet A, Proix N, Billon G, Recourt P, Ouddane B. 2007. Environmental impacts of heavy metal discharges from a smelter in Deûle-canal sediments (Northern France): concentration levels and chemical fractionation. Water Air Soil Pollut. 180(1):83-95.

Brismar T. 1998. Thallium transport in cellular membranes. In: Nriagu JO. ed. Thallium in the environment. New York, NY, USA, John Wiley and Sons. p 241-261.

Buccafusco RJ, Ells SJ, LeBlanc GA. 1981. Acute toxicity of priority pollutants to bluegill (*Lepomis macrochirus*). Bull Environm Contam Toxicol. 26:446-452.

Callahan MA, Slimak MW, Gabel NW, May IP, C.F. Fowler CF. 1979. Water-related environmental fate of 129 priority pollutants. Vol. I. U.S. Environmental Protection Agency. Office of Water Planning and Standards, Office of Water and Waste Management. Washington, DC.

Calleja MC, Persoone G, Geladi P. 1994. Comparative acute toxicity of the first 50 multicentre evaluation of In Vitro cytotoxicity chemicals to aquatic non-vertebrates. Arch Environ Contam Toxicol. 26:69-78.

Campanella B, D'Ulivo A, Ghezzi L, Onor M, Petrini R, Bramanti E. 2018. Influence of environmental and anthropogenic parameters on thallium oxidation state in natural waters. Chemosphere. 196:1-8.

Canada. 2001. Priority Substances List Assessment Report, Releases from Primary and Secondary Copper Smelters and Copper Refineries and Releases from Primary and Secondary Zinc Smelters and Zinc Refineries. Environment Canada and Health Canada.

Canada, Dept. of the Environment. 2012. *Canadian Environmental Protection Act, 1999: Notice with respect to certain substances on the Domestic Substances List* [PDF]. Canada Gazette, Part I, vol. 146, no. 48, Supplement.

Canada, Dept. of the Environment. 2017a. *Canadian Environmental Protection Act, 1999: Notice with respect to certain substances included as part of the 2017 Inventory Update*. Canada Gazette, Part I, vol. 151, no. 2.

Canada. 1999. *Canadian Environmental Protection Act, 1999*. S.C. 1999, c.33. Canada Gazette Part III, vol. 22, no. 3.

Canada. 2003. *Natural Health Products Regulations*. SOR/2003-196.

Canada, Dept. of the Environment. 2017b. Regulations Amending the Metal Mining Effluent Regulations. Canada Gazette, Part I, vol. 151, no. 19.

Carlson RW, Bazzaz FA, Rolfe GL. 1975. The effect of heavy metals on plants II. Net photosynthesis and transpiration of whole corn and sunflower plants treated with Pd, cd, Ni and Tl. Environ Res. 10:113-120.

[CCME] Canadian Council of Ministers of the Environment. 1999. Canadian Water Quality Guidelines for the Protection of Aquatic Life: Thallium [PDF]. Winnipeg (MB): Canadian Council of Ministers of the Environment. [accessed 2019 Jan 31].

[CCME] Canadian Council of Ministers of the Environment. 2006. The Canada-wide standards (CWSs) for mercury emissions from coal-fired electric power generation (EPG) plants [PDF]. Winnipeg (MB): Canadian Council of Ministers of the Environment.

[CCME] Canadian Council of Ministers of the Environment. 2007. A protocol for the derivation of water quality guidelines for the protection of aquatic life [PDF]. Winnipeg (MB): Canadian Council of Ministers of the Environment. [accessed 2019 Jan 31].

[CDC] Centers for Disease Control and Prevention. 2018. Fourth National Report on Human Exposure to Environmental Chemicals[PDF]. Updated Tables, March 2018. Volume 1. U.S. Department of Health and Human Services. Atlanta (GA): CDC. [accessed 2018 Sept].

Cheam V, Lawson G, Lechner J, Desrosiers R, Nriagu J. 1996. Thallium and cadmium in recent snow and firn layers in the Canadian Arctic by atomic fluorescence and absorption spectrometries. Fresenius J Anal Chem. 355:332-335.

Cheam V, Garbai G, Lechner J, Rajkumar J. 2000. Local impacts of coal mines and power plants across Canada. I. Thallium in waters and sediments. Water Qual Res J Can. 35:609–631.

Cheam V, Lechner J, Desrosiers R, Sekerka I, Lawson G, Mudroch A. 1995. Dissolved and total thallium in Great Lakes water. J Great Lakes Res. 21(3):384-394.

Cheam V. 2001. Thallium contamination of water in Canada. Water Qual Res J Can. 36(4):851-878.

Cheminfo Services Inc. 2013. Review of the characteristics of the water effluents and solid wastes from base metals smelting facilities. Final report. Environment Canada Base Metals Smelting Unit. [Internal]

[CIMT] Canadian International Merchandise Trade [Database] [modified 2018 Sept 20] Ottawa (ON): Statistics Canada. [accessed 2018 Sept 20]

Clausen B, Karlog O. 1974. Loading with thallium among wild animals of the marten genus and badgers in Denmark. Nordisk Veterinaer Medicin. 26:339-350 [Cited in Dmowski et al. 2015].

Clausen B, Karlog O. 1977. Thallium loading in owls and other birds of prey in Denmark. Nordisk Veterinaer Medicin. 29:227-231 [Cited in Dmowski et al. 2015].

Cotton FA, Wilkinson G. 1988. Advanced inorganic chemistry. 5th ed. New York, Chichester, Brisbane, Toronto, John Wiley and Sons.

Couillard Y, Grapentine LC, Borgmann U, Doyle P, Masson S. 2008. The amphipod *Hyalella azteca* as a biomonitor in field deployment studies for metal mining. Enviro Pollut. 156:1314-1324.

Couture P, Fortin C, Hare L, Lapointe D, and Pitre D. 2011. Critical Review of Thallium in Aquatic Ecosystems. Environment Canada, Research Report No R-1272. Gatineau, QC.

Cromartie E, Reichel WL, Locke LN, Belisle AA, Kaiser TE, Lamont TG, et al. 1975. Residues of organochlorine pesticides and polychlorinated biphenyls and autopsy data for bald eagles 1971–1972. Pestic Monit J. 9:11-14 [Cited in Dmowski et al. 2015].

Cwynar P, Kolacz R, Grudnik T. 2014. The influence of chronic thallium intoxication on laying hens, including its accumulation in tissues, organs, and eggs. Pol J Environ Stud. 23(3):949-954.

Dawson GW, Jennings AL, Drozdowski D, Rider E. 1976. The acute toxicity of 47 industrial chemicals to fresh and saltwater fishes. J Hazard Mater. 1:303-318.

DelValls TA, Sáenz V, Arias AM, Blasco J. 1999. Thallium in the marine environment: first ecotoxicological assessments in the Guadalquivir estuary and its potential adverse effect on the Doñana European natural reserve after the Aznalcóllar mining spill (SW Spain). Cien Mar. 25(2):161-175.

Dmowski K, Badurek M. 2001. Thallium contamination of selected biotic elements of ecosystems neighboring the zinc smelter in Bukowno. In: Gworek B, Mocek A. eds. Obieg pierwiastków w przyrodzie. Monografia, t 1. Instytut Ochrony Srodowiska, Warszawa. p 19-24.

Dmowski K, Kozakiewicz A, Kozakiewicz M. 1998. Small Mammal Populations and Community under Conditions of Extremely High Thallium Contamination in the Environment. Ecotoxicol Environ Saf. 41(1):2-7.

Dmowski K, Kozakiewicz M, Kozakiewicz A. 2000. Small mammal response at population and community level to heavy metal pollution (Pb, Cd, Tl). In: Kammenga J, Laskowski R. wyd. Demography in ecotoxicology. John Wiley & Sons. Chichester, New York. p 113-125.

Dmowski K, Rossa M, Kowalska J, Krasnodębska-Ostręga B. 2015. Thallium in spawn, juveniles, and adult common toad (Bufo bufo) living in the vicinity of a zinc-mining complex, Poland. Environ Monit Assess. 187(4141):1-8.

[DPD] Drug Product Database [database]. [modified 2018 June 12]. Ottawa (ON): Health Canada. [accessed 2018 Sept 18].

Duan L, Song J, Li X, Yuan H, Li N, Xu Y. 2012. Thallium concentrations and sources in the surface sediments of Bohai Bay. Mar Environ Res. 73:25-31.

Dumas J, Hare L. 2008. The internal distribution of nickel and thallium in two freshwater invertebrates and its relevance to trophic transfer. Environ Sci Technol. 42:5144-5149.

Dvornikov AG, Ovsyannikov LB, Sidenko OG. 1973. [Biogeochemical dispersion haloes of chalcophyllite elements in gold ore manifestations of the Nagolnyi Ridge (The Donbas).] Dopov Akad Nauk Ukr RSR (in Russian). B35:490-494 [Cited in IPCS 1996].

Dvornikov AG, Ovsyannikova LB, Sidenko OG. 1976. [Some characteristics of the coefficients of biological absorption and the biogeochemical coefficients at hydrothermal deposits of the Donets Basin in relation to predicting hidden ore mineralization.] Geokhimiya (in Russian). 4:626-633 [Cited in IPCS 1996].

[ECCC, HC] Environment and Climate Change Canada, Health Canada. [modified 2017 March 12]. Categorization of chemical substances. Ottawa (ON): Government of Canada. [accessed 2019 January 20].

[ECCC] Environment and Climate Change Canada. 2016. Guide for Reporting to the National Pollutant Release Inventory (NPRI) 2016 and 2017: Canadian Environmental Protection Act, 1999 (CEPA).

[ECCC] Environment and Climate Change Canada. 2016a. Thallium in Canadian municipal wastewater and biosolids. CMP Research and Monitoring Section. Science and Risk Assessment Directorate, Environment Canada. p 2. Unpublished data. Gatineau (QC): ECCC.

[ECCC] Environment and Climate Change Canada. 2018. National Fish Contaminants Monitoring and Surveillance Program. Unpublished data. Gatineau (QC): ECCC.

[ECCC] Environment and Climate Change Canada. 2018a. Deriving predicted no-effect concentrations using an assessment factor approach. Unpublished document. Gatineau (QC): ECCC. .

[ECCC] Environment and Climate Change Canada. 2018b. Supporting documentation: Potassium as a potential Toxicity Modifying Factor (TMF). Gatineau (QC): ECCC. Information in support of the draft screening assessment for Thallium and its compounds.

[ECCC] Environment and Climate Change Canada. 2018c. Taking action to phase out coal power. Taking action to phase out coal power. Gatineau (QC): ECCC.

Ecoscape Environmental consultants Ltd. and Larratt Aquatic Consulting Ltd. 2014. Lower Columbia River aquatic receiving environment monitoring program for Teck Trail operations. Contract No.: 932600-OS. Ecoscape File No. 12-976.2.

[EEM] Environmental Effects Monitoring. 2018. Measured concentrations of total thallium in exposed and reference waterbodies collected under the Metal Mining Effluent Regulations from 2005 to 2015. Gatineau (QC): Environment and Climate Change Canada. [accessed 2016 Jul 26]. [restricted access].

Environment Canada. 2013a. Wastewater treatment plant data collected under the Chemicals Management Plan Environmental Monitoring and Surveillance Program. Data collected 2009-2012. Unpublished data. Gatineau (QC): Environment Canada.

Environment Canada. 2013b. DSL Inventory Update data collected under the Canadian Environmental Protection Act, 1999, section 71: Notice with respect to certain substances on the Domestic Substances List. Data prepared by: Environment Canada, Health Canada; Existing Substances Program.

Environment Canada. 2013. Federal Environmental Quality Guidelines: Hydrazine. Gatineau (QC): Environment Canada.

Environment Canada. 1996. Seedling emergence and earthworm toxicity tests on barium and thallium. Ecosystem Conservation Directorate, Evaluation and Interpretation Branch, Guidelines Division, Ottawa. Unpublished data [Cited in CCME 1999].

Environment Canada. 1998. Canadian soil quality guidelines for thallium: Environmental. Supporting document - Final draft. October 1998. Environmental Quality Branch, Guidelines and Standards Division, Ottawa [Cited in CCME 1999].

Fard NJH, Javid AZ, Ravanbakhsh M, Ramezani Z, Ahmadi M, Angali KA, Ardeshirzadeh S. 2017. Determination of nickel and thallium concentration in Cynoglossus arel fish in Musa estuary, Persian Gulf, Iran. Environ Sci Pollut Res. 24:2936-2945.

Ferronato C, Carbone S, Vianello G, Antisari LV. 2016. Thallium toxicity in Mediterranean horticultural crops (*Fragaria vesca* L., *Mentha pulegium* L., *Ocimum basilicum* L.). Water Air Soil Pollut. 227:375.

Fischer E, Molnar L. 1997. Growth and reproduction of *Eisenia fetida* (oligochaete, *Lumbricidae*) in semi-natural soil containing various metal chlorides. Soil Biol Biochem. 29(3/4):667-670.

Frantz G, Carlson RM. 1987. Effects of rubidium, cesium, and thallium on interlayer potassium release from Transvaal vermiculite. Soil Sci Soc Am J. 51(2):305-308.

Frattini P. 2005. Thallium properties and behaviour – A literature study. Geological Survey of Finland. S41/0000/2005/2. Espoo. p 46.

Galvan-Arzate S, Santamaria A. 1998. Mini-review: Thallium toxicity. Toxicol Lett. 99:1-13.

Gantner N, Power M, Babaluk JA, Reist JD, Kock G, Lockhart LW, Solomon KR, Muir DCG. 2009. Temporal trends of mercury, cesium, potassium, selenium and thallium in arctic char (*Salvelinus alpinus*) from lake Hazen, Nunavut, Canada: effects of trophic position, size and age. Environ Toxicol Chem. 28(2):254-63.

Gao Y, Leermakers M, Elskens M, GBillon G, Ouddane B, Fischer J-C, Baeyens W. 2007. High resolution profiles of thallium, manganese and iron assessed by DET and DGT techniques in riverine sediment pore waters. Sci Total Environ. 373:526-533.

Geilmann W, Neeb KH. 1959. [Application of the evaporation analysis for minor amounts of material. II. The proof and determination of minor contents of thallium.] Fresenius Z Anal Chem. (in German). 165: 251-268 [Cited in IPCS 1996].

German Federal Environment Agency. 2011. Substance monograph on thallium – Reference and human biomonitoring (HBM) values for thallium in urine. Human Biomonitoring Committee of the Federal Environment Agency. Bundesgesundheitsbl 54: 516-524. With permission of Springer

Harvey C, Mackay D, Webster E. 2007. Can the unit world model concept be applied to hazard assessment of both organic chemicals and metal ions? Environ Toxicol Chem. 26(10):2129-2142.

Hassler CS, Chafin RD, Klinger MB, Twiss MR. 2007. Application of the biotic ligand model to explain potassium interaction with thallium uptake and toxicity to plankton. Environ Toxicol Chem. 26(6):1139-1145.

Hays SM, Aylward LL, Gagne M, Nong A, Krishnan K. 2010. Biomonitoring Equivalents for inorganic Arsenic. Regul Toxicol Pharmacol 58(1):1-9.

Hébert M, Lemyre-Charest D, Gagnon G, Messier F, de Grosbois S. 2011. Agricultural land application of municipal biosolids: PBDE and metal levels in cow's milk [PDF].

Health Canada. [modified 2011 January 31]. Dietary Intakes of Contaminants and Other Chemicals for Different Age-Sex Groups of Canadians – Canadian Total Diet Study – Health Canada [modified 2011 Jan 31]. Ottawa(ON): Government of Canada. [accessed 2018 Oct 1].

Health Canada. 2013. Second Report on Human Biomonitoring of Environmental Chemicals in Canada. Results of the Canadian Health Measures Survey Cycle 2 (2009-2011). Ottawa (ON): Government of Canada.

Health Canada. 2016. Science Approach Document. Biomonitoring-based Approach 2 for Barium-containing Substances, Molybdenum-containing Substances, Silver-containing Substances, Thallium-containing Substances and Inorganic Tin-containing Substances. Ottawa (ON): Government of Canada. [accessed 2019 January 21].

Health Canada. [modified 2017a August 10]. Results of the Prioritization of the Revised In Commerce List. Ottawa (ON): Government of Canada [accessed 2017 Dec 5].

Heim M, Wappelhorst O, Markert B. 2002. Thallium in terrestrial environments - occurrence and effects. Ecotoxicology. 11:369-377.

Heitmuller PT, Hollister TA, Parrish PR. 1981. Acute toxicity of 54 industrial chemicals to sheepshead minnows (*Cyprinodon variegatus*). Bull Environm Contam Toxicol. 27:596-604.

Henke R, Eberius M, Appenroth K-J. 2011. Induction of frond abscission by metals and other toxic compounds in *Lemna minor*. Aquat Toxicol. 101:261-265.

Horne JD, Swirsky MA, Hollister TA, Oblad BR, James H Kennedy JH. 1983. Aquatic toxicity studies of five priority pollutants. Final Report. Report Number 4398. Houston, TX. NUS Corporation. Prepared for the USEPA.

Hou LP, YangY, Shu H, Ying GG, Zhao JL, Chen YB, Chen YH, Fang GZ, Li X, Liu JS. 2017. Changes in histopathology, enzyme activities, and the expression of relevant genes in Zebrafish (*Danio rerio*) following long-term exposure to environmental levels of thallium. Bull Environ Contam Toxicol. Published on line: DOI 10.1007/s00128-017-2176-5.

[HSDB] Hazardous Substances Data Bank [database]. 1983- . Search results for Thallium Compounds. Bethesda (MD): National Library of Medicine (US). [updated 2009 Apr 16; accessed 2018 Jul 01].

Huber F, Kirchmann H. 1978. Biomethylation of Tl (I) compounds. Inorg Chem Acta. 29:L249-L250 [Cited in IPCS 1996].

Ikemoto T, Tu NPC, Okuda N, Akihisa Iwata A, Omori K, Tanabe S, Tuyen BC, Takeuchi I. 2008. Biomagnification of trace elements in the aquatic food web in the Mekong Delta, South Vietnam using stable carbon and nitrogen isotope analysis. Arch Environ Contam Toxicol. 54:504-515.

[IPCS] International Programme on Chemical Safety. 1996. Environmental Health Criteria 182: Thallium. Geneva, Switzerland, World Health Organization. [accessed 2016 Feb 11].

[IRIS] Integrated Risk Information System. 2009. Thallium (I), soluble salts CASRN Various [PDF]. U.S Environmental Protection Agency, National Center for Environmental Assessment [Accessed April 2016].

Kabata-Pendias A, Pendias H. 1992. Trace elements in soils and plants. CRC Press, 2rd edition. Florida. p 365.

Karbowska B. 2016. Presence of thallium in the environment: sources of contaminations, distribution and monitoring methods. Environ Monit Assess. 188:640.

Kazantzis G. 1979. Thallium. In: Handbook on the toxicology of metals. Edited by Friberg L, Nordberg GF, Vouk VB. Ch. 36. Elsevier/North-Holland Biomedical Press, Amsterdam.

Kazantzis G. 2000. Thallium in the environment and health effects. Environ Geochem Health. 22:275-280.

Kilgour & Associates Ltd. 2016. Estimating background concentration ranges data to inform ecological chemical risk assessments. Unpublished report. Gatineau (QC): Environment and Climate Change Canada, Ecological Assessment Division. (manuscript in preparation).

Kilic V, Altunsoy F, Kilic GA. 2011. Effect of thallium on the survival and morphology of *Tubifex tubifex* (oligochaete, *Tubificidae*). Fresen Environ Bull. 20(9a):2442-2445.

Kimball GL. 1978. The effects of lesser known metals and one organic to fathead minnow (*Pimephales promelas*) and *Daphnia magna*. Minneapolis MN. University of Minnesota, Department of Entomology, Fisheries and Wildlife. Report No. N:88.

Krasnodebska-Ostręga B, Dmowski K, Stryjewska E, Golimowski J. 2005. Determination of thallium and other toxic elements (As, Cd, Cu, Mn, Pb, Se, Sb, and Zn) in water and sediment samples from the vicinity of the zinc-lead smelter in Poland. J Soils Sediments. 5:71-73.

Krasnodębska Ostręga B, Golimowski J. 2008. Zielona gałązka, która truje - Thallus. Analityka: nauka i praktyka, 1:46-50 [Cited in Karbowska 2016].

Kwan KHM, Smith S. 1988. The effect of thallium on the growth of *Lemna minor* and plant tissue concentrations in relation to both exposure and toxicity. Environ Pollut. 52:203-219.

LeBlanc GA, Dean JW. 1984. Antimony and thallium toxicity to embryos and larvae of fathead minnows (*Pimephales promelas*). Bull Environ Contam Toxicol. 32:565-569.

Leblanc M, Robinson BH, Petit D, Deram A, Brooks RR. 1999. The phytomining and environmental significance of hyperaccumulation of thallium by *Iberis intermedia*. Econ Geol. 94:109-114.

LaCoste C, Robinson B, Brooks R. 2001. Uptake of thallium by vegetables: its significance for human health, phytoremediation, and phytomining. J Plant Nutr. 24(8):1205-1215.

Laforte L, Tessier A, Gobeil C, Carignan R. 2004. Thallium diagenesis in lacustrine sediments. Geochim Cosmochim Acta. 69(22): 5295-5306.

Lachover D, Plaut M, and Angel-Malachi S. 1958. Some effects of thallium sulfate on plant growth, and its behavior in the soil. Ministry of Agriculture, State of Israel, KTAVIM, Records of the Agricultural Research Station. 8(1-2):1-10 [Cited in CCME 1999].

Lan CH, Lin TS. 2005. Acute toxicity of trivalent thallium compounds to *Daphnia magma*. Ecotoxicol Environ Saf. 61(3):432-435.

Lapointe D, Couture P. 2009. Influence of the route of exposure on the accumulation and subcellular distribution of nickel and thallium in juvenile fathead minnows (*Pimephales promelas*). Arch Environ Contam Toxicol. 57:571-580.

Lapointe D, Couture P. 2010. Accumulation and effects of nickel and thallium in early-life stages of fathead minnows (*Pimephales promelas*). Ecotoxicol Environ Saf. 73:572-578.

Lapointe D, Sophie G, Ponton D, Hare L, Couture P. 2009. Influence of prey type on nickel and thallium assimilation, subcellular distribution and effects in juvenile fathead minnows (*Pimephales promelas*). Environ Sci Technol. 43:8665-8670.

LeBlanc GA, Dean JW. 1984. Antimony and thallium toxicity to embryos and larvae of fathead minnows (*Pimephales promelas*). Bull Environ Contam Toxicol. 32:565-569.

LeBlanc GA. 1980. Acute toxicity of priority pollutants to water flea (*Daphnia magna*). Bull Environ Contain Toxicol. 24:684-691.

Leblanc M, Petit D, Deram A, Robinson BH, Brooks RR. 1999. The phytomining and environmental significance of hyperaccumulation of thallium by *Iberis intermedia* from Southern France. Econ Geol. 94(1):109-113.

Lee AG. 1971. The Chemistry of Thallium. Elsevier, New York, 1971. p 336

Lide DR. (ed.). 2005. CRC Handbook of Chemistry and Physics. 86th ed. Boca Raton, FL: CRC Press Inc. p. 2661. Internet version: http://www.hbcponline.com/. Last accessed: December 13th, 2018.

Lin TS, Meier P, Nriagu J. 2005. Acute toxicity of thallium to *Daphnia magna* and *Ceriodaphnia dubia*. Bull Environ Contam Toxicol. 75:350-355.

Lin TS, Nriagu J, Wang XQ. 2001. Thallium concentration in lake trout from Lake Michigan. Bull Environ Contam Toxicol. 67:921-925.

Lin TS, Nriagu JO. 1998. Speciation of thallium in natural waters. Nriagu JO. ed. In: Thallium in the environment. John Wiley & Sons, Inc.: New York. Vol. 29. p 31-43.

Lin TS, Nriagu JO. 1999. Thallium speciation in the Great Lakes. Environ Sci Technol. 33:3394-3397.

[LNHPD] Licensed Natural Health Products Database [database]. [modified 2018 Feb 6]. Ottawa (ON): Health Canada. [accessed 2018 Sept 18].

Lukaszewski Z, Jakubowska M, Zembrzuski W. 2018. The mobility of thallium from bottom soil of the Silesian-Cracowian zinc-lead ore deposit region (Poland). J Geochem Explor. 184:11-16.

Madejon P. 2013. Chapter 23: Thallium. Alloway BJ. ed. In: Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. Environmental Pollution 22. Springer Science Business Media Dordrecht. p 7.

McConnell JR, Edwards R. 2008. Coal burning leaves toxic heavy metal legacy in the Arctic. PNAS. 105(34):12140-12144.

McCool MM. 1933. Effect of thallium sulphate on the growth of several plants and on nitrification in soils. Contrib. Boyce Thompson Inst. 5:289-296 [Cited in CCME 1999].

McGeer JC, Brix KV, Skeaff JM, Deforest DK, Brigham SI, Adams WJ, Green A. 2003. Inverse relationship between bioconcentration factor and exposure concentration for metals: Implications for hazard assessment of metals in the aquatic environment. Environ Toxicol Chem. 22:1017-1037.

McNeely RN, Neimanis VP, Dwyer L. 1979. Thallium. In: Water quality sourcebook. A guide to water quality parameters. Environment Canada, Inland Waters Directorate, Water Quality Branch, Ottawa.

[MDMER] Metal and Diamond Mining Effluent Regulations 2018. Metal and Diamond Mining Effluent Regulation (SOR-2002-222). [last amended 2018 Dec 17, accessed 2019 Apr 10].

Mochizuki M, Mori M, Akinaga M, Yugami K, Oya C, Hondo R, Ueda F. 2005. Thallium contamination in wild ducks in japan. J wildl Dis. 41(3):664-668.

Mulkey JP, Oehme FW. 1993. A review of thallium toxicity. Vet Human Toxicol. 35:445-451.

Munch B, Clausen B, Karlog O. 1974. Thallium poisoning in red foxes (*Vulpes vulpes*) and badgers *(Meles meles)* in Denmark. Nordisk Veterinaer Medicin. 26:323–338 [Cited in Dmowski et al. 2015].

[NAPS] National Air Pollution Surveillance Network. 2011. NAPS Data Products Data Sets: 2011 IntegratedPM2.5_Final.zip. Ottawa (ON): Government of Canada. [modified 13 Jul 7; accessed 2015 Dec 23].

Naumann B, Eberius M, Appenroth K-J. 2007. Growth rate based dose-response relationships and EC-values of ten heavy metals using the duckweed growth inhibition test (ISO 20079) with *Lemna minor* L. clone St. J Plant Physiol. 164:1656-1664.

Nautilus Environmental. 2016. Effects characterization of selected inorganic moieties. Submitted to: Gatineau, Environment Canada.

[NHPID] Natural Health Products Ingredients Database [database]. [modified 2019 Jan 18]. Ottawa (ON):Health Canada. [accessed 2018 Sept 18].

Nolan A, Dirk Schaumlo D, Lombi E, Ouerdane L, Lobinski R, McLaughlin M. 2004. Determination of Tl(I) and Tl(III) by IC-ICP-MS and application to Tl speciation analysis in the Tl hyperaccumulator plant *Iberis intermedia*. J Anal At Spectrom. 19:757 – 761.

Norwood WP, Borgmann U, Dixon DG. 2007. Chronic toxicity of arsenic, cobalt, chromium and manganese to *Hyalella azteca* in relation to exposure and bioaccumulation. Environ Pollut. 147:262-272.

[NPRI] National Pollutant Release Inventory [database]. 2017. Search results for CAS RN NA – 37. Gatineau (QC): Environment and Climate Change Canada. [updated 2017 Sept 14; accessed 2018 Jan 10].

OMEE (Ontario Ministry of Environment and Energy). 1993. Ontario typical range of chemical parameters in soil, vegetation, moss bagsand snow. Version 1.0a. PIBS 2792. Standards Development Branch, Phytotoxicology Section, Toronto [Cited in CCME 1999].

Ofukany AFA, Wassenaar LI, Bond AL, Hobson KA. 2014. Defining fish community structure in Lake Winnipeg using stable isotopes (δ^{13}C, δ^{15}N, δ^{34}S): Implications for monitoring ecological responses and trophodynamics of mercury & other trace elements. Sci Total Environ. 497-498:239-249.

Onikura N, Nakamura A, Kishi K. 2008. Acute toxicity of thallium and indium toward brackish-water and marine organisms. J Fac Agr. Kyushu Univ. 53(2):467-469.

Ouellet JD, Dube MG, Niyogi S. 2013. The influence of food quantity on metal bioaccumulation and reproduction in fathead minnows (*Pimephales promelas*) during chronic exposures to a metal mine effluent. Ecotoxicol Environ Saf. 91:188-197.

Pavlíčková J, Zbíral J, Smatanová M, Houserová P, Čižmárová E, Havlíková Š, Kubáň V. 2005. Uptake of thallium from artificially and naturally contaminated soils into Rape (*Brassica napus* L.). J Agric Food Chem. 53:2867-2871.

Pavoni E, Petranich E, Adami G, Baracchini E, Crosera M, Emili A, Lenaz D, Higueras P, Covelli S. 2017. Bioaccumulation of thallium and other trace metals in *Biscutella laevigata* nearby a decommissioned zinc-lead mine (Northeastern Italian Alps). J Environ Manag. 186:214-224.

Peter ALJ, Viraraghavan T. 2005. Thallium: a review of public health and environmental concerns. Environ Int. 31:493-501.

Pickard J, Yang R, Duncan B, McDevitt CA, Eickhoff C. 2001. Acute and sublethal toxicity of thallium to aquatic organisms. Bull Environ Contam Toxicol. 66:94-101.

Proulx CL, Kilgour BW, Francis AP, Bouwhuis RF, Hill JR. 2018. Using a conductivity-alkalinity relationship as a tool to identify surface waters in reference condition across Canada. Water Qual Res J Can. 50(2):1-10.

Pu G, Zhang D, Zeng D, Xu G, Huang Y. 2017. Effects of thallium stress on photosynthesis, chlorophyll fluorescence parameters and antioxidant enzymes activities of Coix Lacryma-jobi. J Environ Sci Eng A. 6:15-21.

Quierolo F, Stegen S, Contreras-Ortega C, Ostapczuk P, Queirolo A, Paredes B. 2009. Thallium levels and bioaccumulation in environmental samples of Northern Chile: human health risks. J Chil Chem Soc. 54(4):464-469.

Radić S, Cvjetko P, Glavas K, Roje V, Pevalek-Kozlina B, Pavlica M. 2009. Oxidative stress and DNA damage in broad bean (Vicia faba L.) seedlings induced by thallium. Environ Toxicol Chem. 28(1):189-196.

Ralph L, Twiss MR. 2002. Comparative toxicity of thallium(I), thallium(III), and cadmium(II) to the unicellular alga Chlorella isolated from Lake Erie. Bull Environ Contam Toxicol. 68:261-268.

Ramsden D. 2002. Thallium. Mol Death. 304-311.

Rasmussen et al. 2016. Preliminary Exposure Data for Five Metals from 2014-2017 CMP(3) Research. February 15, 2016. Ottawa (ON): Exposure and Biomonitoring Division, Health Canada [personal communication, unpublished data].

Reimann CP, de Caritat P. 1998. Chemical Elements in the Environment. Edited by Springer-Verlag, Berlin, Germany. ISBN 3-540-63670-6. p 398.

Rickwood CJ, King M, Huntsman-Mapila P. 2015. Assessing the fate and toxicity of Thallium I and Thallium III to three aquatic organisms. Ecotoxicol Environ Saf.115:300–308.

Sager M. 1994. Thallium. Toxicol. Environ. Chem. 45:11-32.

Sánchez-Chardi A. 2007. Tissue, age, and sex distribution of thallium in shrews from Doñana, a protected area in SW Spain. Sci Total Environ. 383:237-240.

Scheckel KG, Lombi E, Rock SA, Mclaughlin MJ. 2004. In Vivo synchrotron study of thallium speciation and compartmentation in *Iberis intermedia*. Environ Sci Technol. 38:5095-5100.

Schedlbauer OF, Heumann KG. 2000. Biomethylation of thallium by bacteria and first determination of biogenic dimethylthallium in the ocean. Appl Organometal Chem. 14:330-340.

Schlekat CE, McGeer JC, Blust R, Borgmann U, Brix KV, Bury N, Couillard Y, Dwyer RL, Luoma SN, Robertson S, Sappington KG, Schoeters I, Sijm DTHM. 2007. Bioaccumulation: hazard identification of metals and inorganic metal substances. In: Adams WJ, Chapman PM. eds. Assessing the hazard of metals and inorganic metal substances in aquatic and terrestrial systems. SETAC Publications, CRC Press. Chap 4:55-87.

Schoer J. 1984. Thallium. In: Hutzinger O, editor. Handbook of Environmental Chemistry, vol. 3. New York, Springer-Verlag. p 143-214.

Sherstobitov AO, Lapin AA, Glazunov VV, Nikiforov AA. 2010. Transport of monovalent thallium across the membrane of oocyte of the Lamprey Lampetra fluviatilis. J Evol Biochem Physiol. 46(3):235-240.

Siegel BZ, Siegel SM. 1975. A selective role for potassium in the phytotoxicity of thallium. Bioinorg Chem. 4:93-97.

Smith S, Kwan KHM. 1989. Use of aquatic macrophytes as a bioassay method to assess relative toxicity, uptake kinetics and accumulated forms of trace metals. Hydrobiologia. 188/189:345-351.

Sun J, Zou X, Ning Z, Sun M, Peng J, Xiao T. 2012. Culturable microbial groups and thallium-tolerant fungi in soils with high thallium contamination. Sci Total Environ. 441:258-264.

Sun J, Zou X, Xiao T, Jia Y, Ning Z, Sun M, Liu Y, Jiang T. 2015. Biosorption and bioaccumulation of thallium by thallium-tolerant fungal isolates. Environ Sci Pollut Res. 22:16742-16748.

Tatsi K, Turner A, Handy RD, Shaw BJ. 2015. The acute toxicity of thallium to freshwater organisms: Implications for risk assessment. Sci Total Environ. 536:382-390.

Thomson AJ, Breton J, Butt JN, Hatchikian EC, Armstrong FA. 1992. Iron-sulphur clusters with labile metal ions. J Inorg Biochem. 47:197-207.

Tugulea AM et al. 2016. National survey of disinfection by-products and selected drinking water contaminants in Canadian drinking water (2009-2010) [personal communication, unpublished data].

Turner A, Cabon A, Glegg GA, Fisher AS. 2010. Sediment–water interactions of thallium under simulated estuarine conditions. Geochim Cosmochim Acta. 74:6779-6787.

Turner A, Furniss O. 2012. An evaluation of the toxicity and bioaccumulation of thallium in the coastal marine environment using the macroalga, *Ulva lactuca*. Mar Pollut Bull. 64:2720-2724.

Turner A, Pilsburry A. 2013. Accumulation of aqueous and dietary thallium by the marine snail, Littorina littorea. Estuar Coast Shelf Sci. 129:73-76.

Twining BS, Fisher NS. 2004. Trophic transfer of trace metals from protozoa to mesozooplankton. Limnol Oceanogr. 49:28-39.

Twining BS, Twiss MR, Fisher NS. 2003. Oxidation of thallium by freshwater plankton communities. Environ Sci Technol. 37:2720-2726.

Twiss MR, Twining BS, Fisher NS. 2003. Partitioning of dissolved thallium by seston in Lakes Erie and Ontario. Can J Fish Aquat Sci. 60:1369-1375.

Twiss MR, Twining BS, Fisher NS. 2004. Bioconcentration of inorganic and organic thallium by freshwater phytoplankton. Environ Toxicol Chem. 23(4):968-97.

[USGS] United States Geological Survey. 2018. Mineral Commodity Summary. Thallium [PDF] Reston (VA): US Geological Survey [accessed 2018 Sept 18]

Urík M, Kramarová Z, Ševc J, Čerňanský S, Kališ M, Medveď J, Littera P, Kolenčík M, Gardosova K. 2010. Biosorption and bioaccumulation of thallium(I) and its effect on growth of *Neosartorya fischeri* strain. Polish J of Environ Stud. 19(2):457-460.

Vaněk A, Chrastný V, Mihaljevič M, Drahota P, Grygar T, Komárek M. 2009. Lithogenic thallium behavior in soils with different land use. J Geochem Explor. 102(1):7-12.

Vanek A, Grosslova Z, Mihaljevic M, Ettler V, Chrastny V, Komarek M, Tejnecky V, Drabek O, Penizek V. 2015a. Thallium contamination of soils/vegetation as affected by sphalerite weathering: a model rhizospheric experiment. J Hazard Mater. 283:148-156.

Vaněk A, Grösslová Z, Mihaljevič M, Trubač J, Ettler V, Teper L, Cabala J, Rohovec J, Zádorová T, Penížek V, Pavlů L, Holubík O, Němeček K, Houška J, Drábek O, Ash C. 2015b. Isotopic tracing of thallium contamination in soils affected by emissions from coal-fired power plants. Environ Sci Technol. 50:9864−9871.

Vink BW. 1993. The behaviour of thallium in the (sub)surface environment in terms of Eh and pH. Chem Geol. 109:119-123.

Wallace WG, Luoma SN. 2003. Subcellular compartmentalization of Cd and Zn in two bivalves. II. Significance of trophically available metal (TAM). Mar Ecol Prog Ser. 257:125-137.

Wang C, Chen Y, Liu JL, Wang J, Li X, Zhang Y, Liu Y. 2013. Health risks of thallium in contaminated arable soils and food crops irrigated with wastewater from a sulfuric acid plant in western Guangdong province, China. Ecotoxcol Environ Saf. 90:76-81.

[WEAO] Water Environment Association of Ontario. 2010. Assessing the Fate and Significance of Microconstituents and Pathogens in Sewage Biosolids. Update of the 2001 WEAO Report on 24 Fate and Significance. Prepared for the WEAO by Hydromantis, Webber Environmental and Parker W. p 206 [Cited in Hebert et al. 2011].

Wierzbicka M, Szarek-Łukaszewska G, Grodińska K. 2004. Highly toxic thallium in plants from the vicinity of Olkusz (Poland). Ecotoxcol Environ Saf. 59:84-88.

Xiao T, Guha J, Boyle D, Liu CQ, Chen J. 2004b. Environmental concerns related to high thallium levels in soils and thallium uptake by plants in southwest Guizhou, China. Sci Total Environ. 318:223-244.

Xiao T, Guha J, Boyle D, Liu CQ, Zheng B, Wilson GC, Rouleau A, Chen J. 2004a. Naturally occurring thallium: a hidden geoenvironmental health hazard? Environ Int. 30:501-507.

Zitko V, Carson WV. Carson WG. 1975a. Thallium: occurrence in the environment and toxicity to fish. Bull Environ Contam Toxicol. 13:23-30.

Zitko V. 1975. Toxicity and pollution potential of thallium. Sci Total Environ. 4:185-192.

Appendix A. Acute toxicity studies for thallium in freshwater

Table A-1. Key acute aquatic toxicity studies considered in choosing a critical toxicity value for freshwater for thallium

Group	Test organism	Endpoint	Value [b] (µg/L)	Reference
Fish	Bluegill (*Lepomis macrochirus*)	96 h LC$_{50}$	125 857 [a]	Buccafusco et al. 1981; Dawson 1976
Fish	Fathead minnow (*Pimephales promelas*)	96 h LC$_{50}$	1 800	Kimball 1978
Fish	Zebrafish (*Danio rerio*)	96 h LC$_{50}$	870	Tatsi et al. 2015
Fish	Rainbow trout (*Oncorhynchus mykiss; Salmo gairdneri*)	96 h LC$_{50}$	3 134 [a]	Horne et al. 1983; Pickard et al. 2001
Invertebrates	Amphipod (*Hyalella azteca*)	7 d LC$_{50}$	12	Borgmann et al. 1998
Invertebrates	Amphipod (*Gammarus minus*)	96 h LC$_{50}$	100	Horne et al. 1983
Invertebrates	Snail (*Physa heterostropha*)	96 h LC$_{50}$	2 500	Horne et al. 1983
Invertebrates	Harlequin fly (*Chironomus riparius*)	96 h LC$_{50}$	148 000	Belowitz et al. 2014
Invertebrates	Oligochaete (*Tubifex tubifex*)	96 h LC$_{50}$	18	Kilic et al. 2011
Invertebrates	Rotifer (*Brachionus calyciflorus*)	24 h LC$_{50}$	7 680	Calleja et al. 1994
Invertebrates	Water flea (*Daphnia magna*)	48 h LC$_{50}$	1 608 [a]	Kimball 1978; LeBlanc 1980; Lin et al. 2005; Pickard et al. 2001
Invertebrates	Water flea (*Daphnia pulex*)	48 h EC$_{50}$	725	Tatsi et al. 2015
Invertebrates	Water flea (*Ceriodaphnia dubia*)	48 h LC$_{50}$	660	Lin et al. 2005
Algae	Green algae (*Pseudokirchneriella subcapitata*)	48 h EC$_{50}$ growth rate	37	Tatsi (personal communication, 2017)

[a] Geometric means applied for the SSD data points.

[b] The toxicity endpoints listed are for Tl(I). If the thallium speciation was not specified in the study, it was assumed to be Tl(I). Endpoints were converted to µg/L if original data was reported in mg/L.