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Assessment

Thallium and its compounds

Environment and Climate Change Canada
Health Canada

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Canada

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Synopsis

Pursuant to section 68 of the *Canadian Environmental Protection Act, 1999* (CEPA), the Minister of the Environment and the Minister of Health have conducted an assessment of thallium and its compounds. The scope of this assessment covers the thallium moiety and considers all thallium-containing substances that may release thallium, as well as thallium in its elemental form and thallium released to the environment in dissolved, solid, or particulate forms.

The Chemical Abstracts Service Registry Numbers (CAS RN[1]), the *Domestic Substances List* (DSL) or Revised In Commerce List (R-ICL) names and the common names of thes 5 substances identified as initial thallium priorities 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	Thallium	Thallium
563-68-8	Acetic acid, thallium(1+) salt	Thallium(I) acetate
7791-12-0	Thallium chloride	Thallium chloride
10031-59-1[a]	Sulfuric acid, thallium(1+) salt (1:?)	Thallium(I) sulfate
55172-29-7[b]	Thallium chloride (^{201}TlCl)	^{201}TlCl

[a] This substance was removed from the R-ICL in 2022 as it was determined not to have commercial activity in Canada for use in products under the *Food and Drugs Act.*

[b] This substance is on the Revised In Commerce List (R-ICL).

Thallium exists in the earth's crust at an average concentration of 0.7 parts per million. 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 in trace amounts in most living organisms.

Anthropogenic sources of thallium are primarily associated with the incidental production and releases of residues or by-products from various industrial activities, such as smelting and refining processes, metal mining, and fly ashes from coal-fired electrical power generation. Thallium production was estimated to be below 8 tonnes globally in 2020.

Thallium(I) acetate, thallium chloride, and thallium(I) sulfate were included in a survey issued pursuant to section 71 of CEPA. In 2011, between 100 kg and 1000 kg of thallium chloride were manufactured in Canada; no information above the reporting

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threshold of 100 kg was received with respect to the import of this substance in Canada. No information above the reporting threshold of 100 kg was received for the other two substances. According to the Canadian International Merchandise Trade (CIMT) database, less than 50 kg per year of thallium was imported into Canada between 2017 and 2020.

Internationally, the main uses of thallium substances include use in fibre (optical) glasses to increase refractive index and density, in semiconductor material, in infrared radiation detection and transmission equipment, in photoelectric cells, in mercury-thallium alloys for low-temperature measurements, in crystalline filters for light diffraction in acoustic-optical measuring devices, in high-density liquid for sink-float separation of minerals, as an activator in gamma radiation detection devices (scintillometers), and as intermediates in chemical production. Other uses include use in mercury arc lamps, alloys with other metals, jewellery, fireworks, and pigments and dyes. Additional uses of thallium in Canada are in products available to consumers, for example, 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 the manufacture of food packaging materials.

Thallium exists in two oxidation states in the aquatic environment: monovalent thallous Tl(I) (that is, Tl^{+}) and trivalent thallic Tl(III) (that is, 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 assessment.

Thallium is considered to be 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. Thallium is not an essential element for organisms. Organisms exposed to thallium readily take up thallium either through direct contact with environmental media (dermal or respiratory exposure) or by food ingestion. Elevated thallium concentrations have been observed in organisms living near sources of releases (for example, smelters). Thallium may also accumulate in aquatic and soil-dwelling organisms and plants. Owing to the very limited and contradictory data presently available, no conclusions can be drawn with certainty regarding the potential for thallium to biomagnify in aquatic and terrestrial food chains.

At very low concentrations, thallium causes mortality as well as growth and reproductive effects on both aquatic and terrestrial organisms. The chronic predicted no-effect concentrations (PNECs) for thallium for aquatic organisms were derived from ecotoxicity studies. The soil PNEC was adopted from the 1999 Canadian Council of Ministers of the Environment (CCME) guideline as current thallium soil toxicity data indicate that this PNEC is protective of soil-dwelling organisms and plants in the Canadian environment.

The potential for cumulative effects was considered in this assessment by examining cumulative exposures to the moiety of thallium. A weight of evidence approach was used to determine the potential for ecological harm in Canada. Risk quotient (RQ) analyses were performed by comparing predicted environmental concentrations (PECs) with PNECs. Thallium releases to the aquatic compartment from metal mining, base metals smelting, coal-fired power generation facilities, and wastewater treatment systems were analyzed. The PECs for the metal mining and base metals smelting sectors consisted primarily of measured thallium concentrations in the receiving environments (that is, exposure areas) and corresponding reference areas. The analysis indicates that thallium releases from most facilities are limited, but there is a potential for harm to the aquatic environment as a result of thallium release from a small number of facilities in these sectors. Prior to the year 2000, one facility in the coal-powered energy sector had a high RQ owing to releases of thallium from its lagoon effluents; however, the latest release and effluent concentration data from the National Pollutant Release Inventory (NPRI) showed low potential for ecological risk from the facility. RQs for thallium discharged to surface water from wastewater treatment systems or through the application of biosolids to agriculture lands from wastewater treatment systems are low.

Considering all available lines of evidence presented in this assessment, there is risk of harm to the environment from thallium and its compounds. It is concluded 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 concluded 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.

For the assessment of risk to human health, thallium and its compounds were evaluated using the Biomonitoring-based Approach 2, which compares human biomonitoring data (as a measure of exposure) against biomonitoring guidance values (health-based exposure guidance values) to assess if substances are of low concern for human health. Thallium concentrations were measured in the urine of North Americans as part of the Canadian Health Measures Survey (CHMS) and the National Health and Nutrition Examination Survey (NHANES) in the United States as well as in studies targeting specific subpopulations, such as a First Nations Gwich'in community in Old Crow, Yukon, First Nations communities in the Northwest Territories Mackenzie Valley, and the Inuit population in Nunavik, Quebec. A human biomonitoring guidance value (HBM-I) established by the German Environmental Agency is considered to be protective of adverse health effects of thallium in humans. Median and 95th percentile urinary thallium concentrations in Canadians (3 to 79 years) of 0.21 µg/g and 0.55 µg/g creatinine were lower than the HBM-I value of 6.4 µg/g creatinine. In addition, urinary thallium concentrations in certain Indigenous communities were below the HBM-I value. Therefore, thallium and its compounds are considered to be of low concern to human health at current levels of exposure.

The human health assessment took into consideration those groups of individuals within the Canadian population who, due to greater susceptibility or greater exposure, may be more vulnerable to experiencing adverse health effects. For thallium and its compounds, Canadian human biomonitoring data in children as well as in pregnancies and specific Indigenous communities were used to inform consideration of these populations and take them into account in the risk assessment outcomes.

Considering all the information presented in this assessment, it is concluded 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 concluded that thallium and its compounds meet one or more of the criteria set out in section 64 of CEPA.

It is also determined that thallium and its compounds meet the persistence criteria but not the bioaccumulation criteria as set out in the *Persistence and Bioaccumulation Regulations* of CEPA.

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1. Introduction

Pursuant to section 68 of the *Canadian Environmental Protection Act, 1999* (CEPA) (Canada 1999), the Minister of the Environment and the Minister of Health have conducted an 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 or were prioritized through other mechanisms 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 assessment focuses on the thallium moiety[3] 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 (for example, chloride). Throughout this assessment, the term “thallium” refers to both elemental thallium and its compounds unless otherwise indicated. Consequently, the assessment 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 takes into consideration combined exposure to the thallium moiety, whether the thallium moiety is present in environmental media (for example, water, sediment, soil, air), and thallium-containing food or products that may originate from natural or anthropogenic sources.

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

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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 taking steps to address them for potential impact on human health and the environment in order to risk-manage the substances, if required.

[3] For the purpose of this document, “moiety” signifies a part of a molecule. A moiety is a discrete chemical entity, identified from a parent compound or its transformation products, that is expected to have toxicological significance.

concentrations were differentiated from concentrations attributed to anthropogenic sources.

This assessment includes the consideration of information on physical-chemical properties, environmental fate, hazards, uses, releases, and exposures. Relevant data were identified up to November 2021. Empirical data from key studies were critically reviewed and used to reach the conclusions. When available and relevant, information presented in assessments from other jurisdictions was also considered.

This 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 of Toxicology Excellence for Risk Assessment (TERA) and from Judy LaKind of LaKind Associates during the development of the Biomonitoring-based 2 Science Approach Document. Additionally, the draft of this assessment (published September 19, 2020) was subject to a 60-day public comment period. While external comments were taken into consideration, the final content and outcome of the assessment remain the responsibility of Health Canada and Environment and Climate Change Canada.

Assessments focus on information critical to determining whether substances meet the criteria as set out in section 64 of CEPA by considering scientific information, including information, if available, on subpopulations who may have greater susceptibility or greater exposure, vulnerable environments and cumulative effects[4], and by incorporating a weight of evidence approach and precaution.[5] This assessment presents the critical information and considerations on which the conclusion is based.

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[4] The consideration of cumulative effects under CEPA may involve an analysis, characterization and possible quantification of the combined risks to health or the environment from exposure to multiple chemicals.

[5] The 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 that is based on the criteria contained in section 64 of CEPA does not preclude actions being taken under other sections of CEPA or other acts.

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 1998b).

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 elemental form and thallium released in the environment in dissolved, solid, or particulate forms, including five thallium-containing substances that were identified as initial thallium priorities for assessment.

The Chemical Abstracts Service Registry Numbers (CAS RN[6]), DSL or R-ICL names, and common names for the five substances are presented in Table 2-1.

Table 2-1. Substance identities

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[c]	Sulfuric acid, thallium (1+) salt (1:?) (Thallium sulfate)[c]	Tl_2SO_4	504.83
55172-29-7[b,d]	Thallium chloride (^{201}TlCl)	$^{201}TlCl$	236.42

[a] This substance is highly reactive when exposed to moisture in air and will release bioavailable thallium ions under environmental conditions.

[b] This substance was included in this assessment as it was identified for further consideration following prioritization of the Revised In Commerce List (R-ICL).

[c] This substance was removed from the R-ICL as it was determined not to have commercial activity in Canada for use in products under the *Food and Drugs Act* (Health Canada [modified 2022]).

[d] Radioactive

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3. Physical and chemical properties

Thallium metal is insoluble in water but is highly reactive. When exposed to air and moisture, the surface of the metal oxidizes to form a coating of thallium oxide, and 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; IPCS 1996; CCME 1999; Frattini 2005).

The ionic radii and the electronegativity constant of Tl(I) are similar to those of alkali metals (for example, potassium), whereas thallic compounds are less basic, resembling aluminium (Frattini 2005). The water solubility of thallous salts generally ranges from soluble to very soluble (Table 3-1), except for the sulfide (Tl_2S, $pK_{sp} = 20$) (Lide 2005). The solubility of Tl(III) compounds (for example, $Tl(OH)_3$, $pK_{sp} = 45.2$) in water is generally low and dependent on pH; soluble Tl(III) ions can exist only under extremely acidic conditions (Lin and Nriagu 1998a).

A summary of the physical and chemical property data (ATSDR 1992; IPCS 1996; Lide 2005) available for the thallium-containing substances identified as 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 (ATSDR 1992; IPCS 1996; Lide 2005)

Property	Thallium	Thallium(I) acetate	Thallium(I) chloride	Thallium sulfate
CAS RN	7440-28-0	563-68-8	7791-12-0, 55172-29-7	10031-59-1
Color	Bluish white	White	Colourless	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 0.7 parts per million (USGS 2021). 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 at levels of up to 1000 mg/kg (Kazantzis 2000). Thallium is also present in many minerals (for example, 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 de Caritat 1998), but these minerals are rare (HSDB 1983-; IPCS 1996; CCME 1999). 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 in residues of the smelting and refining process; from sulfuric 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 2021). World reserves of thallium contained in zinc resources are estimated to be on the order of 17 million kilograms; these reserves are mostly located in Canada, Europe, and the United States. World reserves in coal resources are estimated at 630 million kilograms (USGS 2021).

In 2020, global thallium production was estimated to be less than 8 tonnes (USGS 2021).

Thallium(I) acetate, thallium chloride, and thallium(I) sulfate(CAS RN 563-68-8, 7791-12-0, and 10031-59-1) have been included in surveys issued pursuant to section 71 of CEPA (Canada 2012, 2017a). In 2011, between 100 kg and 1000 kg of thallium chloride were manufactured in Canada; no information was received above the 100 kg reporting threshold with respect to the import of this substance in Canada (Environment Canada 2013b). No information above the reporting threshold of 100 kg was received for the two other substances.[7] According to the CIMT database, less than 50 kg per year of thallium (as unwrought, powders, and articles thereof) were imported into Canada between 2017 and 2020 (Statistics Canada [modified 2021]). In 2022, thallium(I) sulfate was removed from the R-ICL as it was determined to have no commercial activity in Canada for use in products under the *Food and Drugs Act* (Health Canada [modified 2022]).

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[7] 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).

4.3 Uses

Internationally, the main uses of thallium substances include use in fibre (optical) glasses to increase refractive index and density, in photoelectric cells, as an activator in gamma radiation detection devices (scintillometers), in semiconductor material, in infrared radiation detection and transmission equipment, in crystalline filters for light diffraction in acoustic-optical measuring devices, in mercury-thallium alloys for low-temperature measurements, in high-density liquid for sink-float separation of minerals, and as intermediates in chemical production (ATSDR 1992; Peter and Viraraghavan 2005; USGS 2021). Other uses include use in mercury arc lamps, alloys with other metals, jewellery, fireworks, and pigments and dyes, as well as for impregnation of wood and leather against fungi and bacteria (ATSDR 1992; CCME 1999; Peter and Viraraghavan 2005; USGS 2021). In addition, the radioactive isotope thallium-201 is used in imaging of the heart to determine the location and extent of coronary artery blockages as well as scar tissue from previous heart attacks (Blumenthal et al. 2013). Thallium salts were also used in the past as pesticides (bactericides, rodenticides, and insecticides) and as a depilatory agent to treat various diseases such as fungal infections, syphilis, tuberculosis, and gonorrhea. These historical uses have, however, been banned in most countries owing to thallium's high toxicity, accumulation in the human body, and persistence in the environment (Peter and Viraraghavan 2005). In Canada, thallium sulfate-based insecticides for ants were the only registered agricultural use, but these were completely discontinued in 1974 (Lang 1993 as cited in CCME 1999, personal communication information provided by Agriculture Canada, Ottawa; unreferenced). 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 ingredient in licensed natural health products[c]	Y

Abbreviations: Y = yes, use was reported for this substance.

[a] Personal communication, email 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 through the weathering of minerals and rocks that contain thallium (CCME 1999). Soil erosion, forest fires, and volcanic activity can also contribute to natural releases of thallium into the aquatic environment (Couture et al. 2011).

Since 2014, Canadian facilities have been required to 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 total environmental releases of thallium to the NPRI between 2014 and 2020 (NPRI 2021). During this period, the number of facilities reporting thallium increased from 15 to 50, and total yearly releases of thallium and its compounds to the environment via air, water, and land ranged from 1243 kg to 3569 kg.

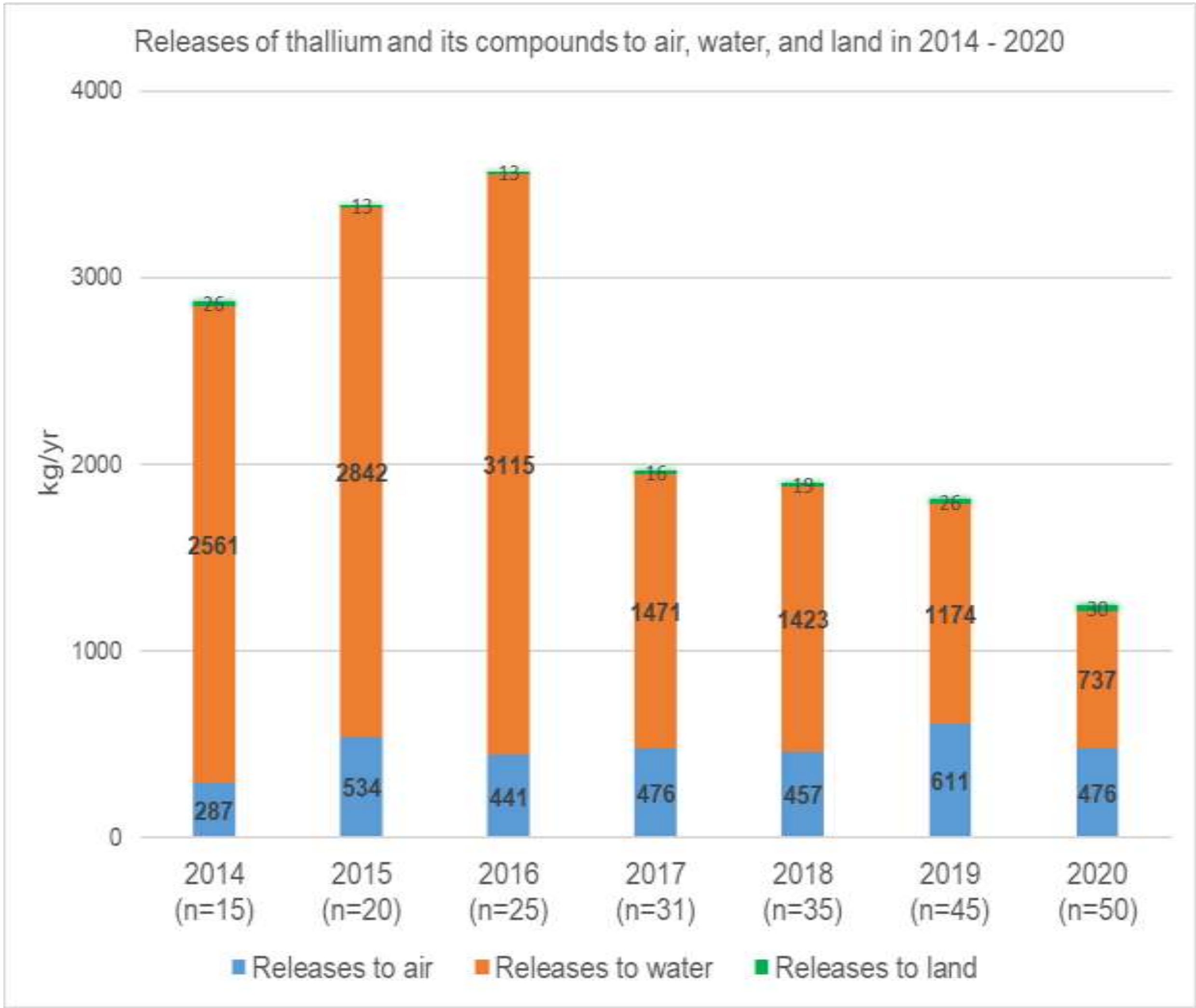

Figure 5-1. NPRI data on releases of thallium and its compounds (kg per year) to water, air, and land from 2014 to 2020

***[Long description:** Figure 5-1 summarizes NPRI data on releases of thallium and its compounds (kg per year) to water, air, and land from 2014 to 2020*[a]

Report year	***Number of reports***	***Releases to air***	***Releases to water***	***Releases to land***	***Total releases***
2014	*15*	*287*	*2561*	*26*	*2874*
2015	*20*	*534*	*2843*	*13*	*3390*
2016	*25*	*441*	*3115*	*13*	*3569*
2017	*31*	*476*	*1471*	*16*	*1963*
2018	*35*	*456*	*1423*	*19*	*1898*
2019	*45*	*611*	*1174*	*26*	*1811*
2020	*50*	*476*	*737*	*30*	*1243*

*[a] Quantities are rounded up to the nearest 1 kg.***]**

Figure 5-2 depicts the total yearly releases of thallium to air greater than 1 kg by industrial sector, including cement and concrete product manufacturing, coal mining, coal-fired power generating plants (electric power generation, transmission, and distribution), metal ore mining, and base metals smelters (non-ferrous metal [(except aluminum] production and processing), between 2014 and 2020 (NPRI 2021). Base metals smelters reported the highest releases of thallium to air, followed by metal ore mining. The reported thallium emissions to air from metal ore mining came largely from two facilities, which emitted a total of 267 kg of thallium in 2020 compared to 317 kg from the entire metal ore mining sector. The thallium released to air from these two facilities is associated with the operation of induration furnaces from the iron ore pelletizing (IOP) plants.

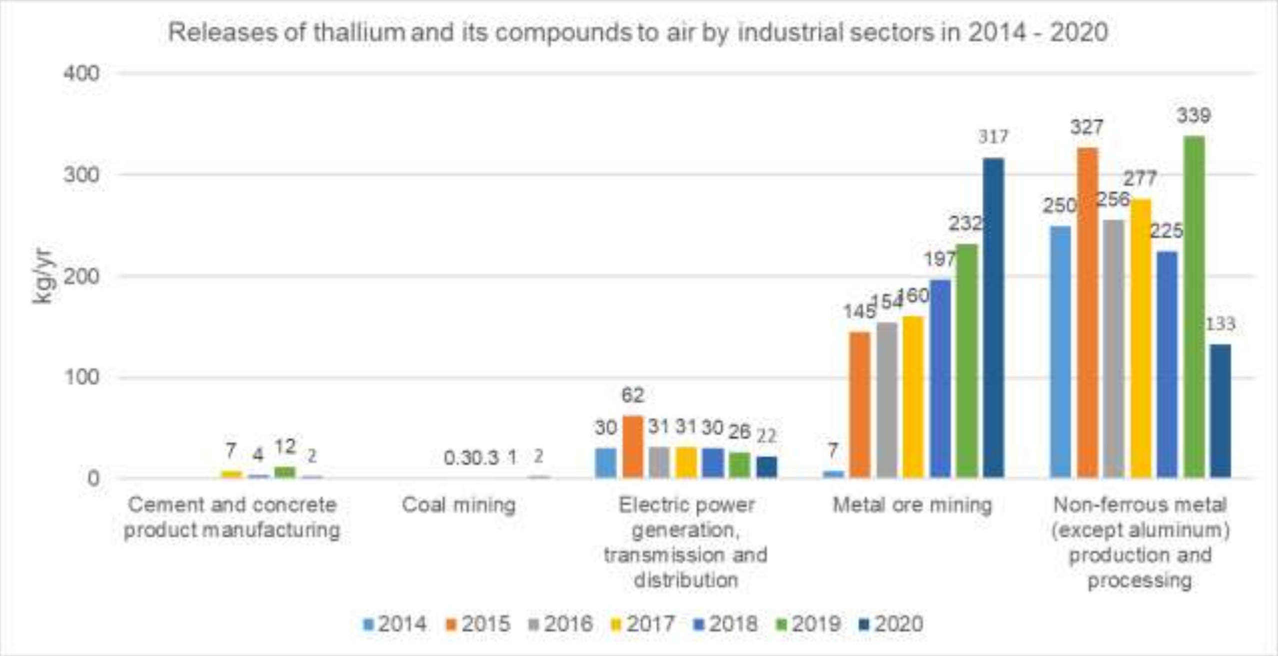

Figure 5-2. NPRI data on releases of thallium and its compounds (kg per year) to air by industrial sector from 2014 to 2020

***[Long description:** Figure 5-2 summarizes NPRI data on releases of thallium and its compounds (kg per year) to air by industrial sector from 2014 to 2020*[a]

Report year	*Cement and concrete product manufacturing*	*Coal mining*	*Electric power generation, transmission, and distribution*	*Metal ore mining*[b]	*Non-ferrous metal (except aluminum) production and processing*
2014	*NR*	*NR*	*30*	*7*	*250*
2015	*NR*	*NR*	*62*	*145*	*327*
2016	*NR*	*NR*	*31*	*154*	*256*
2017	*7*	*0.3*	*31*	*160*	*277*
2018	*4*	*0.3*	*30*	*197*	*225*

Report year	***Cement and concrete product manufacturing***	***Coal mining***	***Electric power generation, transmission, and distribution***	***Metal ore mining[b]***	***Non-ferrous metal (except aluminum) production and processing***
2019	*12*	*1*	*26*	*232*	*339*
2020	*2*	*2*	*22*	*317*	*133*

Abbreviations: NR, not reported (no quantities were reported from the sector for thallium releases to air for the calendar year).

[a] The following industrial sectors reported thallium releases to air of less than 1 kg per year during the reporting period: iron and steel mills and ferro-alloy manufacturing, oil and gas extraction, petroleum and coal product manufacturing, and non-metallic mineral mining and quarrying.

[b] Metal ore mining includes the IOP sector, which accounted for a high percentage of the releases by the sector in 2019 and 2020.]

Figure 5-3 depicts the total yearly releases of thallium to water greater than 1 kg by industrial sector, including coal mining, metal ore mining, base metals smelters (non-ferrous metal [except aluminum] production and processing), petroleum and coal product manufacturing, and water, sewage, and other systems between 2014 and 2020 (NPRI 2021). Base metals smelters reported the highest releases of thallium to water compared to other industrial sectors. Thallium can also end up in wastewaters from the use and/or disposal of pharmaceuticals, manufacturing dyes, fireworks, and through wash-off from chemical reactions (Couture et al. 2011). The high levels of thallium reported by one wastewater treatment system in 2014 and 2015 were estimated using half the detection limit for non-detected measurements. In 2016, this facility removed thallium from their list of reportable substances as there had been “no results above the method detection limit (MDL) in two years” (NPRI 2021).

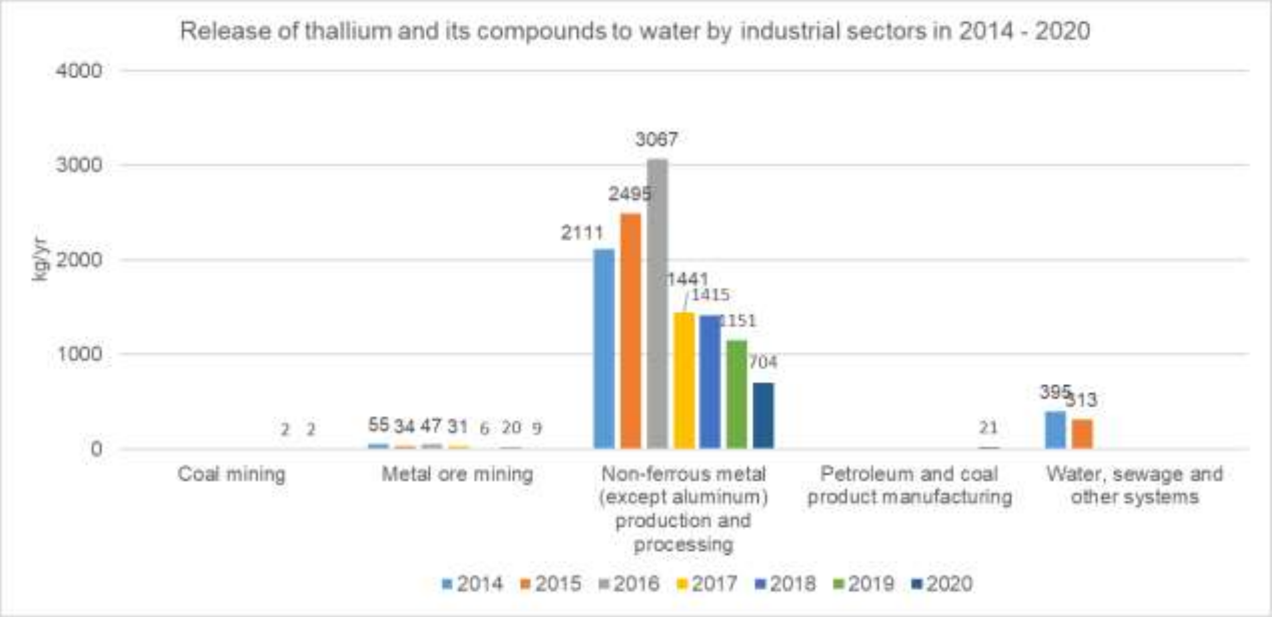

Figure 5-3. NPRI data on releases of thallium and its compounds (kg per year) to water by industrial sector from 2014 to 2020

[Long description: *Figure 5-3 summarizes NPRI data on releases of thallium and its compounds (kg per year) to water by industrial sector from 2014 to 2020*[a]

Report year	*Coal mining*	*Metal ore mining*	*Non-ferrous metal (except aluminum) production and processing*	*Petroleum and coal product manufacturing*	*Water, sewage, and other systems*
2014	*NR*	*55*	*2111*	*NR*	*395*
2015	*NR*	*34*	*2495*	*NR*	*313*
2016	*NR*	*47*	*3067*	*NR*	*NR*
2017	*NR*	*31*	*1441*	*NR*	*NR*
2018	*NR*	*6*	*1415*	*NR*	*NR*
2019	*2*	*20*	*1151*	*NR*	*NR*
2020	*2*	*9*	*704*	*21*	*NR*

Abbreviations: NR, not reported (no quantities were reported from the sector for thallium releases to water for the calendar year).

[a] *The following industrial sectors reported thallium releases to water of less than 1 kg/year during the reporting period: electric power generation, transmission and distribution, pulp, paper, and paperboard mills, and oil and gas extraction.***]**

The metal ore mining sector reported the highest releases of thallium to land, that is, between 13 kg to 28 kg per year from 2014 to 2020. The oil and gas extraction and pulp, paper, and paperboard mills sectors reported between 0.4 kg and 1.5 kg per year of land releases of thallium and its compounds in 2019 and 2020. Other sectors reported less than 1 kg per year or no thallium releases to land (NPRI 2021).

In addition to the industrial sectors that reported to the NPRI, the production of potash fertilizer and the roasting of pyrite during the production of sulfuric acid are other industrial processes that potentially contribute to the release of thallium into the environment (McNeely et al. 1979; Schoer 1984; IPCS 1996; Cheam 2001). However, thallium quantities from these sources are likely to be below the NPRI reporting threshold. Thallium can also leach out from decades-old accumulations of solid wastes produced by smelters, refineries, and gold-ore mills (Kazantzis 1979, 2000).

6. Environmental fate and behaviour

6.1 Environmental distribution

In air, thallium is removed by precipitation, atmospheric dispersion, and wet/dry depositions after it enters the atmosphere (ATSDR 1992). Thallium emissions through atmospheric deposition have been traced in ice and snow in the Canadian Arctic (Cheam 2001) and are global in scope; for example, they have been reported in snow as far as Antarctica (Baiocchi et al. 1994; McConnell and Edwards 2008). Metallic thallium oxidizes slowly in air, forming thallous oxide on the metal’s surface (Lee 1971). Although thallous chloride is photosensitive (Cotton and Wilkinson 1988), the photochemical reaction of thallium is not considered to be a significant fate process in the atmosphere (ATSDR 1992).

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, and Tl(I) is the more thermodynamically stable form (Kaplan and Mattigod 1998; Lin and Nriagu 1998b; Gao et al. 2007). According to Vink (1993), Tl(I) is the predominant form and is mobile when dissolved in water. 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 Lakes is present as Tl(III). Twining et al. (2003) suggested that the reason for this may be the conversion of Tl(I) to Tl(III) by planktonic bacteria. Photooxidation of Tl(I) in the presence of aqueous cations (for example, Fe(III) or As(V)) could also cause Tl(I) to be converted to Tl(III) in natural waters, as demonstrated by Campanella et al. (2018). According to Cotton and Wilkinson (1988), Tl(III) is extensively hydrolyzed and is dominated by an inert $Tl(OH)_3$ complex that 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 as cited in IPCS 1996). 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 (Schedlbauer and Heumann

2000; Hassler et al. 2007). Considering that there is no known anthropogenic source of DMT, neither its environmental fate nor its ecotoxicity and bioaccumulation potential are considered further in this assessment.

Thallium may partition from water to sediment and adsorb onto clay minerals, iron sulfide clusters, and hydrous metal oxides, for example, manganese oxide (Zitko 1975; Callahan et al. 1979; Frantz and Carlson 1987; ATSDR 1992; Thomson et al. 1992; Bidoglio et al. 1993; Duan et al. 2012). It has also been suggested that the precipitation of Tl(III) hydroxide may be an effective mechanism for removing thallium from water. Precipitated Tl(III) hydroxide may then be reduced to Tl(I) by organic-rich anaerobic sediment or bind with sulfide ions in sediment to form insoluble Tl(I) sulfide (Tl_2S) (IPCS 1996; Laforte et al. 2005; Gao et al. 2007; Turner et al. 2010). The partition coefficients for suspended particles-water (log K_{pw}) and sediment-water (log K_{sw}) of 4.28 and 1.48, respectively, summarized by Harvey et al. (2007), indicate that thallium would 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 or hydroxides, resulting in the surface oxidation of Tl(I) to Tl(III), which is then adsorbed or precipitated as Tl_2O_3. Some studies indicate that thallium sorption by iron oxides and soil organic matter is insignificant (Peter and Viraraghavan 2005; Vaněk 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 (Vaněk et al. 2009).

However, elevated thallium concentrations in soils (caused by natural weathering of certain thallium-rich geological rocks or minerals), which result in high plant accumulation, have been reported in China and the Czech Republic (Xiao 2004b; Pavlícková et al. 2005). Kabata-Pendias and Pendias (1992) also report that anthropogenic thallium in soils has been found to be very soluble, and thus, readily available to plants. This is consistent with the low reported soil-water partitioning coefficient value (log K_{ew}) of 0.68 (Harvey et al. 2007), which indicates that thallium is highly mobile in soils. In studying the 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

It is believed that thallium has a certain potential to travel long distances by air because of its mobility in fine particulate forms (ATSDR 1992). Environmental concentrations of thallium have been reported in environmental media and organisms in various remote, minimally exposed areas, such as the Canadian Arctic and other distant Arctic regions (Baiocchi et al. 1994; Cheam et al. 1996; Cheam 2001; Gantner et al. 2009). McConnell and Edwards (2008) presented a study that examined continuous monthly and yearly averaged thallium deposition records from 1772 to 2003 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 1988), but no evidence indicates that thallium is transformed significantly by photochemical reactions in the atmosphere (Callahan et al. 1979).

Elemental thallium 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). In a study by Twiss et al. (2004), which presented the results of bioavailability of Tl(I) and Tl(III) in the unicellular algae *Chlorella sp*. and the diatom *Stephanodiscus hantzschii*, the concentration of free Tl(I) ion in the test media was close to the total dissolved Tl(I) concentration. Compared to Tl(I), the concentration of Tl(III) as free ion in the test media was extremely low and present mostly as inert $Tl(OH)_3$. Rickwood et al. (2015) also observed a rapid conversion of Tl(III) to Tl(I) in the test solution 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 the fact that thallium speciation in environmental media affects its bioavailability and uptake, studies have shown that dietary uptake also contributes to thallium accumulation in aquatic organisms (Lapointe and Couture 2009, 2010; Lapointe et al. 2009; Ouellet et al. 2013). Dietary assimilation of thallium was found to be significant in juvenile fathead minnow compared to the fish at embryo and larvae stages (Lapointe and Couture 2009; Lapointe et al. 2009). When fish were exposed to thallium via water and diet simultaneously, thallium uptake via water was more rapid than via diet. Rapid induction of iono-regulatory processes in fish gills, which limited thallium uptake and accumulation, as well as activation of regulating mechanisms in fish gut to control diet-borne thallium uptake or elimination, were also reported (Lapointe and Couture 2009; Lapointe et al. 2009).

Thallium bioavailability to soil-dwelling organisms and subsequent uptake by terrestrial plants are influenced by various factors. For plants, these factors are thallium speciation, soil type (and, therefore, soil properties), thallium concentration in soils, plant species, and mobility of thallium in soils (Kazantzis 2000; Xiao et al. 2004a; Pavlícková et al. 2005; Vaněk et al. 2015a, 2015b). Similar to in the aquatic compartment, Tl(I) is the predominant form to be accumulated from soils by the plant root system (Tsakovski et al. 1994; Nolan et al. 2004; Xiao et al. 2004a). Using a sequential extraction scheme, Lukaszewski et al. (2018) investigated the thallium mobility of bottom soil samples (0.8 m to 1.0 m deep) formed over six different lithological backgrounds in Poland. The authors found that a significant percentage of thallium in most soil types is strongly entrapped in the aluminosilicate parent matter, which represents the immobile thallium form, and thus is not available for uptake by soil-dwelling organisms. The exception was in soils containing dispersed sulfide ores (Zn-Pb ores, pyrites, As-Sb ores) that are mobile in soils, which suggests that thallium in soils of natural sulfide ores and anthropogenic sources of the same origin (metal ore mining, base metals smelters, etc.) is a source of the most bioavailable thallium species for uptake by terrestrial organisms.

6.3.2 Bioaccumulation in aquatic organisms

The bioconcentration factor (BCF) and bioaccumulation factor (BAF) approaches for most metals are considered to be of little use for predicting metal accumulation and hazard (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 that estimates metal BCFs or BAFs in the freshwater amphipod *Hyalella azteca* and avoids the above-mentioned dependence on concentration. 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 (for example, thallium) but not to 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 the empirical aquatic BCFs and BAFs produced for thallium by linking BCFs with chronic toxic effects in the freshwater amphipod *Hyalella azteca* (Borgmann et al. 1998; Borgmann et al. 2004; Norwood et al. 2007; Couillard et al. 2008).

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; Norwood et al. 2007; Couillard et al. 2008)

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 Quebec (six sites)	17 days	River waters (Allard River and Colombière River)	1645[b]
Laboratory exposure	7 days	Lake Ontario water[c]	1380[b]
Laboratory exposure	7 days	Reconstructed water with no K^+	7220[b]

Abbreviations: ww, wet weight

[a] The freshwater amphipod *Hyalella azteca* was the test organism used 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 to 8.6.

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

Thallium concentrations in phytoplankton and macrophytes have been reported for few species, and most of these values were obtained in laboratory experiments. The field measurements by Zitko et al. (1975) 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 up to 43.4 mg/kg dw and 162 mg/kg dw of thallium, respectively, at thallium concentrations of 0.7 µg/L to 88.3 µg/L in water. The calculated mean BAF values were 21 500 L/kg dw for moss and in the range of 908 L/kg dw to 1 895 L/kg dw for algae. Higher field BAFs (approximately 8 000 L/kg dw to 82 500 L/kg dw) were obtained by Quierolo et al. (2009) for two species of algae—*Myriophyllum aquaticum* and *Zannichellia palustris*—from water contaminated by the 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).

A study by Kwan and Smith (1988) examined the toxicity and accumulation of thallium in *Lemna minor*. It was demonstrated that thallium uptake increased with exposure concentrations during 10-day laboratory tests. Plant BCF values were very high (6 000 000 L/kg to 88 000 000 L/kg), and the exposure concentrations displayed inverse relationships. The plants showed little to no recovery when moved to thallium-free medium following exposure to 0.5 nmol/L (102 µg/L) of thallium or more. Threshold plant tissue concentrations for *Lemna* were in the range of 960 nmol/g to 1440 nmol/g (196 mg/kg to 294 mg/kg), which was higher than the lethal body burden of approximately 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 the uptake of thallium 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 no effect on time to hatch, embryo survival, or enzyme activities was demonstrated. *Tubifex tubifex* were used as fish prey in both studies and were exposed to thallium-spiked sediment for 21 days. The calculated biota-sediment accumulation factors (BSAFs) were 0.92 to 1.32, similar to that of 0.47 to 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 2018a). Under the program and federal or provincial water monitoring programs, three locations were identified for the generation of thallium monitoring data for both water and fish body concentrations (ECCC 2018a). One of the three locations, identified as potentially enriched by thallium as a result of industrial impact, included two water monitoring stations in the receiving waters, located approximately 5.6 km and 13 km downstream from one of the facility's discharge points. The calculated geometric means of the measured thallium concentrations in water from 2005 to 2013 at the two monitoring stations 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 from 2008 to 2015. The calculated geometric means of thallium whole body concentrations in rainbow trout and walleye were 0.110 mg/kg dw and 0.103 mg/kg dw, while calculated field BAFs ranged from 1100 L/kg ww to 1500 L/kg ww. The other two locations had very low detectable thallium concentrations in water, ranging from below detection limit (DL between 0.001 µg/L and 0.1 µg/L) to 0.02 µg/L. The measured thallium whole body concentrations in fish were in the range of 0.0105 mg/kg dw to 0.0434 mg/kg dw, suggesting that thallium can be accumulated by fish at very low concentrations in water. Because over 80% of the water thallium concentrations were below detection limits, field BAFs were not calculated for either location.

Potential thallium contamination in the marine environment has been considered an emerging issue in industrialized areas. For example, Fard et al. (2017) presented a mean thallium concentration of 0.781 mg/kg ww (0.984 mg/kg dw) in Tonguefish muscle tissue 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% of thallium was accumulated from sea water compared with 15% from diet, indicating that dietary uptake was potentially more important than waterborne exposure. Del-Valls et al. (1999) reported that thallium levels in three estuarine and 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 ranged from 0.25 to 1.93 at measured sediment concentrations of 0.059 mg/kg to 0.080 mg/kg, which is 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 to 4 months of field study. Slightly increased thallium concentrations (0.07 mg/kg dw to 0.20 mg/kg dw) were measured in mullet fish tissues (Del-Valls 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 being the hyper-accumulators for thallium (Leblanc et al. 1999; LaCoste et al. 2001; Al-Najar et al. 2003; Pavlícková et al. 2005; Wang et al. 2013; Baceva et al. 2014; Antisari et al. 2016). Many studies (Leblanc et al. 1999; LaCoste et al. 2001; Al-Najar et al. 2003; Sun et al. 2012, 2015) have suggested that the tolerance of some terrestrial plants toward thallium and its high accumulation in these plant species provide promising potential sources for bio- or phytoremediation and phytomining in thallium-polluted areas.

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

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

Fungi displayed a similar strain-dependant trend toward thallium accumulation. Urík et al. (2010) reported up to 36 mg/kg and 430 mg/kg of thallium accumulation by a fungal strain after exposure to thallium concentrations of 1.0 mg/L 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) also demonstrated that some fungal strains can survive in thallium-contaminated soils and have high thallium biosorption and bioaccumulation ability.

6.3.4 Bioaccumulation in terrestrial animals

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

Dmowski et al. (1998) investigated small mammal populations in a community under conditions of extremely high thallium concentrations near a Zn-Pb smelting and mining complex in the Bukowno-Olkusz region in Poland. Elevated thallium levels (as high as 11 mg/kg to 44 mg/kg) were detected in rodents' kidney and liver from the two sites nearest to the smelter. The site closest to the smelter and nearest to the slagheap had the highest contamination levels. Furthermore, 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 entire small mammal community and adult mice productivity (population density, age structure) at the site were significantly reduced, even when compared to other zinc smelter or highly metal-polluted sites. However, whether the effects observed on the rodents were indicative of potential chronic thallium toxicity alone could not be clearly identified as other stressors, including other trace metals from the smelter and slag, could also have potentially contributed to the cause.

Other terrestrial animals in the same region were also monitored for thallium contamination by Dmowski et al. (1998, 2000, 2001, 2015). High concentrations of thallium were reported in common toad (*Bufo bufo*) spawn, juveniles after metamorphosis, and adults, 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 as cited in Karbowska 2016). In fact, the thallium concentrations in toads were much lower compared to other wild vertebrates with symptoms of acute thallium poisoning (Clausen and Karlog 1974, 1977 as cited in Dmowski et al. 2015; Munch et al. 1974 as cited in Dmowski et al. 2015; Cromartie et al. 1975). The toads also displayed many characteristics demonstrating their adaptation to the adverse environment; no external developmental abnormalities in adult individuals, tadpoles, or juveniles from contaminated ponds were detected. The authors suggested that the toads' gelatinous egg masses or strings may be a significant source of thallium for non-resident predators with no adaptation to high concentrations of thallium.

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

Chronic thallium accumulation in farm animals was also investigated by Cwynar et al. (2014). Eight weeks of exposure to food dosed with thallium caused accumulation in the tissues, internal organs, and eggs of laying hens, and thallium accumulation was correlated with the feed levels and exposure duration. The highest accumulations of thallium were found in the bones, followed by the kidneys, muscles, and liver, indicating that the element was easily absorbed by the gastrointestinal tract and rapidly distributed in the animal. No mortality of hens was observed, but disorders in the homeostasis were observed at the highest dose of 16 mg/kg, the effects of which included increased numbers of white blood cells, creatinine, and hematocrit as well as decreased blood glucose levels. The increase in serum creatinine suggests that high levels of thallium in the kidneys may contribute to impaired renal filtration processes, reducing thallium elimination from the body and leading to further accumulation.

The main source of thallium for aquatic birds is their diet. In Japan, Mochizuki et al. (2005) reported that thallium levels were higher in eight duck species from contaminated sites compared to birds from the study's reference (uncontaminated) sites. No ducks from contaminated sites in the study showed indications of toxic physical effects. Benito et al. (1999) also reported monitoring data on trace elements in the blood of aquatic birds after a mining spill in the wetlands of a national park in Spain but found that thallium was not present in birds at any significant concentration (thallium concentrations were below the 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 particularly at risk for accumulation themselves. This appears to be the case for lower trophic level organisms as they tend to have large quantities of extremely polluted medium in their digestive tracts; they are then consumed by higher trophic level organisms, leading to biomagnification. The research on thallium biomagnification potential is limited, however, and results are sometimes 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. The results of the study showed a direct relationship between thallium and char's trophic position as identified by $\delta^{15}N$,[8] indicating the potential to biomagnify. A similar trend was reported by Lin et al. (2001), who measured thallium concentrations in adult lake trout from Lake Michigan. A correlation was found between trout growth factor (fish weight divided by fish 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

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[8] $\delta^{15}N$ is the stable nitrogen isotope signature. $\delta^{15}N$ is used 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.

thallium among prey cell fractions were used to illustrate the likelihood of thallium availability for uptake and subsequent assimilation by predators (Smith and Kwan 1989; Dumas and Hare 2008; Lapointe and Couture 2009; Lapointe et al. 2009).

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% to 85%) and can thus be readily assimilated by predators or grazers. The trophically available thallium reported in aquatic organisms ranged from 50% in *D. magna* and *T. tubifex* consumed by fathead minnow (Lapointe et al. 2009) to 75% in *C. riparius* consumed by the alderfly (Dumas and Hare 2008), which suggests potential trophic transfer along aquatic food chains. Figure 6-1 illustrates the assimilation efficiency with which thallium is transferred between trophic levels in planktonic and benthic food webs (Twining and Fisher 2004; Dumas and Hare 2008; Lapointe and Couture 2009; Lapointe et al. 2009; Couture et al. 2011).

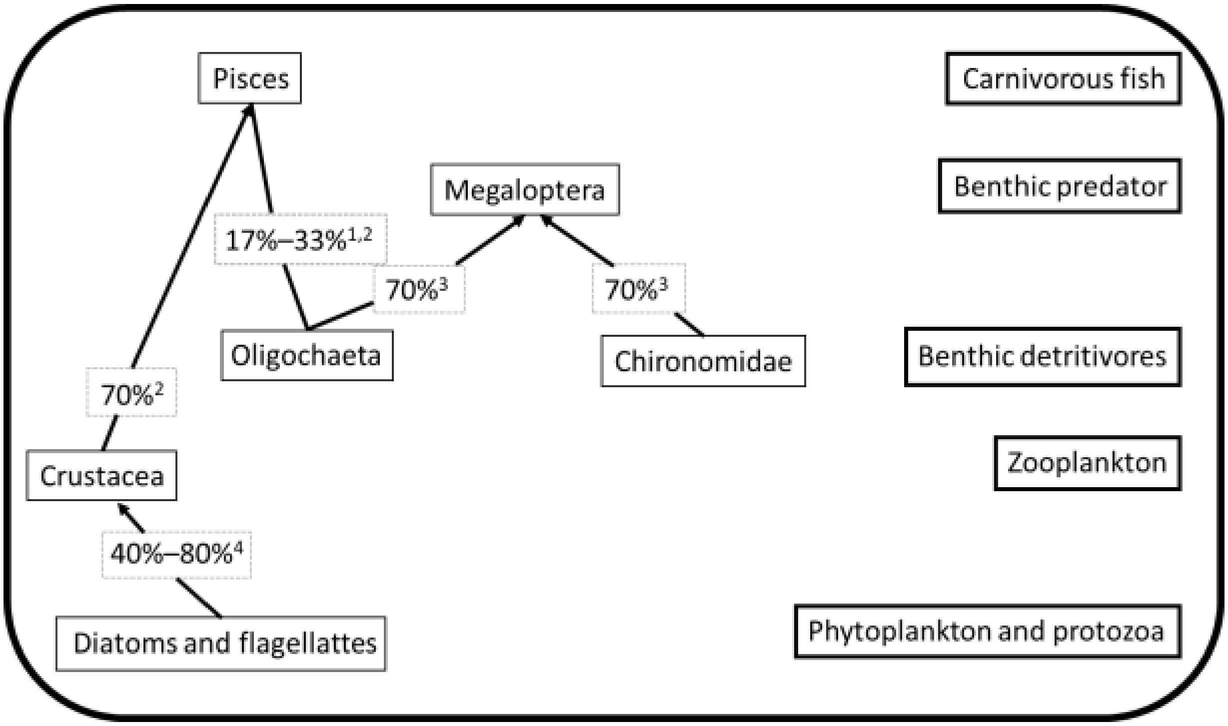

Figure 6-1. Schematic diagram illustrating the assimilation efficiency of thallium transfer between trophic levels in planktonic and benthic food webs (Couture et al. 2011)

[Long description: *Figure 6-1 illustrates thallium assimilation efficiency (AE) transfer among five trophic levels (that is, phytoplankton, zooplankton, benthic detritivores, benthic predator, and carnivorous fish) in planktonic and benthic food webs (Couture et al. 2011). About 40% to 80%[4] of thallium from phytoplanktonic diatoms and flagellates is* *trophically available to zooplanktonic crustacea (Twining and Fisher 2004), while 70%[2] of thallium from crustacea is available to carnivorous fish (Lapointe et al. 2009). Approximately 70%[3] of thallium in benthic detritivores, and 17% to 33%[1,2] of thallium in oligochaeta and chironomidae, is trophically available to benthic predators (that is, Megaloptera) and carnivorous fish, respectively (Lapointe and Couture 2009; Lapointe et al. 2009; Dumas and Hare 2008).**]***

However, contradictory observations were also reported for potential thallium biomagnification in aquatic or terrestrial food chains. No evidence of thallium biomagnification was observed in field studies of various aquatic food webs (Twiss et al. 2003; Ikemoto et al. 2008; Ofukany et al. 2014) and invertebrate subpopulations (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, may be accumulative in both aquatic and terrestrial organisms. Aquatic and terrestrial organisms exposed to thallium readily take up thallium by direct contact with environmental media and/or by food ingestion (Kazantzis 2000; Xiao et al. 2004a; Lin et al. 2005; Pavlícková et al. 2005; Couillard et al. 2008; Lapointe and Couture 2009, 2010; Lapointe et al. 2009; Ouellet et al. 2013; Ecoscape Environmental Consultants Ltd. and Larratt Aquatic Consulting Ltd. 2014; Vaněk et al. 2015a, 2015b). Considerably elevated thallium concentrations in the vicinity of point source areas (for example, smelters) may have an impact on organisms living in such environments (Dmowski and Badurek 2001; Dmowski et al.1998, 2000, 2015). However, essential information is lacking for quantifying the level of thallium tissue residue concentrations associated with adverse effects (for example, effect vs. critical body burden or tissue burden, chronic effects at the subcellular level) as well as for quantifying the thallium detoxification mechanisms and routes of various receptors in the environment.

Considering the limited and contradictory data currently available, thallium biomagnification in both aquatic and terrestrial food chains is uncertain. The subcellular studies mentioned above suggest potential thallium assimilation from lower trophic levels to higher trophic levels in aquatic food chains (Smith and Kwan 1989; Dumas and Hare 2008; Lapointe and Couture 2009; Lapointe et al. 2009). However, contradictory information from the field biomagnification studies warrant further research for the identification of appropriate predator-prey relationships and examination of 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 being researched. The most well known mechanism of thallium toxicity is related to its interference with vital potassium-dependent processes in both aquatic and terrestrial organisms. Owing to the cell membrane's inability to distinguish between thallium and potassium and because they both have similar ionic charges and radii, thallus ion Tl(I) can mimic the biological action of potassium. In certain living systems, Tl(I) has greater affinity for uptake (approximately 10 times greater) 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. Additionally, thallium has been shown to replace potassium ion in the activation of several monovalent cation-activated enzymes, for example, 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; IPCS 1996; Galvan-Arzate and Santamaria 1998).

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 disrupts 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 was 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 the *Iberis* plant (*Brassicaceae* family) was present as free Tl(I) ion within the vascular system but did not accumulate 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). In recent studies of *Lemna minor* plants exposed to Tl(I), thallium was also shown to interfere with molecular and enzymatic antioxidant protective mechanisms (Babić et al. 2009; Radić et al. 2009). The thallium-induced oxidative stress was characterized by the increased production of reactive oxygen species and could also be an important mechanism of thallium toxicity (Radić et al. 2009). In addition, Pu et al. (2017) suggested that the accumulation of thallium in the perennial tropical plant *Coix lacryma-jobi* (*Poaceae* family) inhibited photosynthesis (namely, the photoactivation of Photosystems II[9]). The toxic effects of thallium triggered activation of antioxidant systems (that is, catalase and peroxidase) in the plant, which moderated the adverse effects of thallium.

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

Fish regulate thallium uptake from water via their gills and diet uptake via the gut. This regulation of thallium could be related to potassium 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 to 1 µg/L) for 96 days and demonstrated that thallium 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 zebrafish.

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 involve the excretion of Tl(I) by the renal tubules of the midge or by the binding of sulfur-rich proteins, such as metallothionein, that render Tl(I) inert.

Nagel et al. (2021) reported that after 21 days of thallium exposure, *Daphnia magna* depurated 80% of whole body burden in 8 hours. The authors suggested that excretory mechanisms may exist that allow the organism to rapidly eliminate thallium instead of removing the metal in detoxified form. The thallium body burden over the 21-day exposure did not correlate with changes in potassium concentration. The authors also suggested a likelihood that toxic mechanisms differed among freshwater crustacean species as well as between short- and long-term exposures.

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 acting as a potential TMF for thallium (ECCC 2018b); however, this cannot be reliably confirmed using statistical analyses. A recent study by Nagel et al. (2021) suggested that potassium effects could be species-dependent and differ between short- and long-term exposures. Therefore, the use of potassium as a TMF for freshwater PNEC derivation will not be considered in this assessment.

7.1.3 Effects on aquatic organisms

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

Owing to the speciation and bioavailability of the two thallium redox forms (see section 6.1 of this report), this ecological effects assessment focuses on Tl(I) to evaluate the toxicity of the thallium moiety. It has been shown that the proportion of free Tl(I) is close to the total dissolved Tl(I) concentration in the aquatic environment owing to its low affinity to ligands for the formation of complexes (Lin and Nriagu 1998a; Ralph and Twiss 2002; Lan and Lin 2005; Nagel et al. 2019). Rickwood et al. (2015) also found that Tl(I) was stable, whereas Tl(III) was converted to Tl(I) under experimental conditions during toxicity tests of up to 21 days (Rickwood et al. 2015).

Data on the acute toxicity of thallium to freshwater organisms were compiled and critically reviewed (Nautilus Environmental 2016). Toxicity endpoints and values (from reliable studies) that met the requirements for the derivation of a short-term Type A Canadian Water Quality Guideline (CCME 2007) were summarized in Appendix A (Table A-1). These data were then 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 under comparable test conditions, 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 a 96 h LC_{50} above 100 000 µg/L (Table A-1). With the exception of these species, other freshwater organisms demonstrated a relatively similar range of sensitivity to the toxic effects of thallium, with LC_{50} values ranging from 12 µg/L to 7680 µg/L (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 of less than 24 h with severe effects are generally considered in short-term data sets due to their rapid cell division rate. However, the 48 h LC_{50} for algae growth was selected owing to the growth lag observed in control cultures at 24 h (Tatsi 2017, original endpoint obtained to supplement Tatsi et al. 2015 via personal communication; unreferenced).

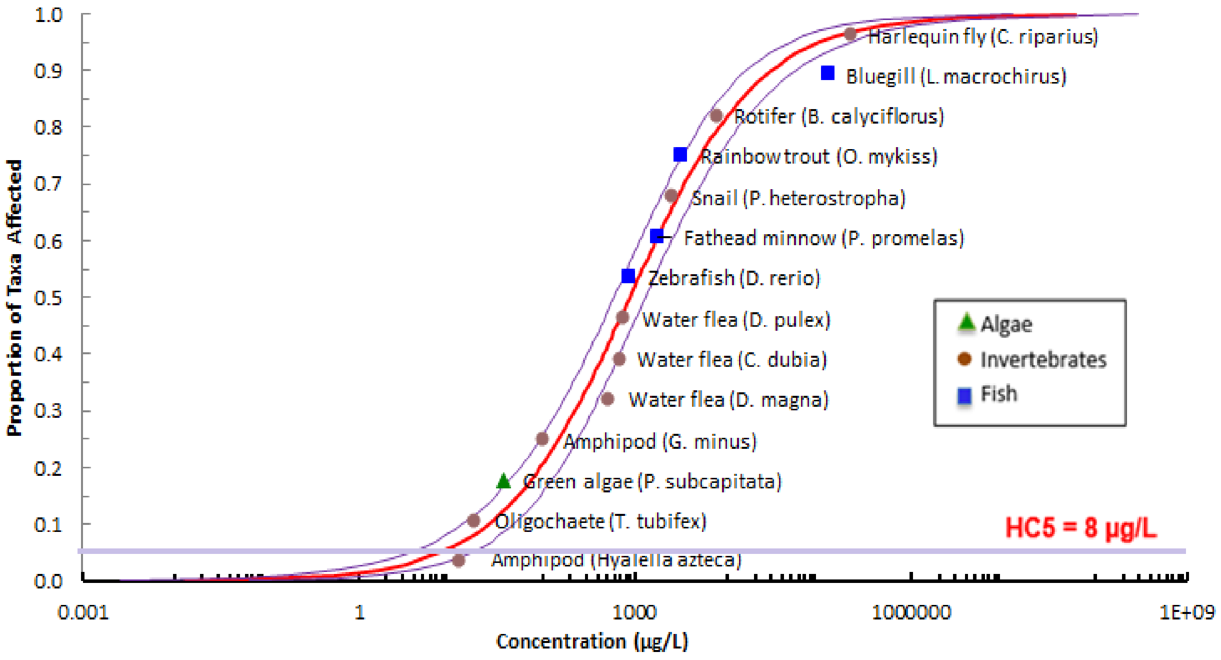

Figure 7-1. Species sensitivity distribution (SSD) for short-term thallium freshwater toxicity

[Long description:** Figure 7-1 illustrates the species sensitivity distribution (SSD), which is based on acute toxicity data for thallium concentrations causing mortality to 50% of the population of freshwater organisms tested. The acute SSD is used to derive the critical toxicity value (CTV) for the thallium short-term effect endpoint for freshwater organisms. The logistic model fit to data is shown on the graph along with the 95% confidence intervals. The 5th percentile of the distribution (HC5) was calculated at 8 µg/L and selected as the short-term CTV for thallium. This figure shows that the sensitivity to thallium of the freshwater organisms tested follows an S-shaped curve.**]

When deriving the SSD, model assumptions and fit were verified with statistical tests. Fit in the lower tail of the SSD Master v3.0 model was calculated by the mean sum of squared error terms (MSE). Normal, logistic, and extreme value models had similar MSEs of 0.0028, 0.0025, and 0.0027, respectively, while the Gumbel model had a higher MSE of 0.0039. The logistic model was selected because it had the lowest MSE, indicating that it had the best fit at the lower end of the SSD curve when compared with the other models. The 5th percentile (HC_5), that is, hazardous concentration for 5% of the freshwater species tested, of the SSD plot was 8 µg/L (Figure 7-1). The HC_5 of 8 µg/L, calculated from the SSD, was 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 thallium. As shown by their acute tolerance to thallium toxicity, freshwater organisms (with the exception of bluegill and harlequin fly) also demonstrated relatively similar ranges of long-term sensitivity to the toxic effects of thallium (that is, LOEC and $E(I)C_{10-25}$ effect values from 1.8 µg/L to 806 µg/L). Owing to the lack of reliable chronic toxicity studies and applicable chronic toxicity data on fish species (Table 7-1) as specified in the CCME protocol (2007), the data set for thallium toxicity is not adequate for a long-term SSD approach.

Table 7-1. Reliable chronic aquatic toxicity studies for freshwater organisms 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
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 and Dean 1984

Common name	Test organism	Endpoint	Value (µg/L)[a]	Reference
Fish	Fathead minnow (*Pimephales promelas*)	30 d EC_{10} weight	69.2	LeBlanc and 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
Invertebrates	Water flea (*Daphnia magna*)	21 d EC_{50} growth	1.6	Nagel et al. 2021
Invertebrates	Water flea (*Daphnia magna*)	21 d EC_{50} reproduction	11.1	Nagel et al. 2021
Invertebrates	Water flea (*Daphnia magna*)	21 d NOEC	0.9	Nagel et al. 2021
Invertebrates	Water flea (*Daphnia magna*)	21 d LOEC growth and reproduction	8.8	Nagel et al. 2021
Invertebrates	Water flea (*Daphnia magna*)	21 d LC_{50}	424–702	Nagel et al. 2021
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

Common name	Test organism	Endpoint	Value (µg/L)[a]	Reference
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
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

Abbreviations: ECx, the concentration of a substance that is estimated to cause some effect on x% of the test organisms; ICx, the concentration of a substance that is estimated to cause an on the test organisms; LC_{50}, median lethal concentration; LOEC, lowest observed effect concentration; NOEC, no observed effect concentration

[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 the original data were 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 sublethal effects, and median to low- or no-effect (Environment Canada 2013c). 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

As a precaution, the $PNEC_{freshwater}$ of 0.8 µg/L was compared to the reliable thallium chronic toxicity endpoints (Table 7-1) to ensure that the organisms would be adequately protected from thallium toxicity over long-term exposure. *Hyalella azteca* was the most sensitive freshwater species tested (Table 7-1), with a 4-week LC_{25} of 2.5 µg/L and a 6-week growth effect EC_{25} of 1.8 µg/L. Rickwood et al. (2015) performed a 21-day reproductive test on adult fathead minnow at thallium concentrations of 8 µg/L and 0.8 µg/L (Table 7-1). Reduced reproductive effects (that is, cumulative spawning) were observed in the 8 µg/L thallium treatments but not in the 0.8 µg/L treatments. Similar effect levels were also observed for *Daphnia magna* (Nagel et al. 2021), with a 21-day

NOEC of 0.9 µg/L for growth and reproductive effects (Table 7-1), which suggests that the long-term freshwater PNEC of 0.8 µg/L is protective.

The thallium PNEC for freshwater organisms is equal to the long-term water quality threshold proposed by the CCME (1999), 0.8 µg/L.

There is limited information on the ecotoxicological effects of thallium in marine water (Table 7-2). It has been suggested that the low thallium (ng/L) and high potassium contents of seawater reduce thallium uptake and toxicity to marine organisms, but high phytotoxicity was observed in certain marine species. Turner and Furniss (2012) investigated the toxicity and bioaccumulation of thallium in the marine macroalga *Ulva lactuca*. The green macroalga showed a high phytotoxicity, with a 48 h LOEC at 10 µg/L in both coastal seawater and estuarine water. Statistical analysis was not performed by the authors; the 48 h EC_{50} values of 20 µg/L for exposure in seawater (salinity of 33 ppt) and 23 µg/L for exposure in estuarine water (salinity of 20 ppt) were estimated via the US EPA TRAP program (Turner and Furniss 2012). The toxicity of thallium to marine algae is in a similar range as the toxicity value for freshwater algae (that is, 48 h EC_{50} of 37 µg/L), although marine algae are more sensitive to the toxic effects of thallium. It has been suggested that the toxicity is associated with thallium uptake through the cell membrane via coupled NaCl/KCl transport, with the uptake rate rising as concentrations of both Na^+ and Cl^- increase (Turner and Furniss 2012). Although rotifers (*Brachionus plicatilis*) are the least sensitive crustaceans to thallium effects, with a 24 h LC_{50} of 100 000 µg/L, the toxicity values for other marine invertebrate species are 3 to 25 times lower (LC_{50} values of 2 400 µg/L to 32 300 µg/L). The available data on the acute toxicity of thallium to marine fish species indicate that the toxicity value falls within a very narrow range of 21 000 µg/Lto 24 000 µg/L (Table 7-2). Marine invertebrates and fish showed a similar or slightly higher tolerance to the toxic effects of thallium compared to freshwater organisms (Table A-1).

The data set for marine water toxicity is inadequate for deriving an SSD (minimum data requirements were not met according to CCME 2007); therefore, an assessment factor approach was used to derive the marine PNEC. Following the assessment factor approach described by Okonski et al. (2021), short- and long-term thallium toxicity data in estuarine and marine water (Table 7-2) were standardized, and the lowest standardized value was selected as the CTV for thallium toxicity in marine water. In this case, the PNEC was derived from the 48 h EC_{50} of 20 µg/L for macroalga (*Ulva lactuca*) in coastal seawater. This was done by dividing the 48 h EC_{50} by an endpoint standardization factor (F_{ES}) of 5 to extrapolate from median effects to low- or no-effect concentrations and by a species variation factor (F_{SV}) of 1. A further mode of action factor (F_{MOA}) of 5 was also applied to account for the specific mode of action (that is, phytotoxicity in marine macroalga). The resulting chronic $PNEC_{\text{marine water}}$ is 0.8 µg/L.

Chronic $PNEC_{\text{marine water}} = CTV \div AF\ (F_{ES} \times F_{SV} \times F_{MOA}) = 20\ \mu g/L \div (5 \times 1 \times 5) = 0.8\ \mu g$ Tl/L

The identical chronic PNEC values derived for fresh and marine water organisms suggest that thallium exerts a similar level of toxicity on 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 thallium.

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 (*Americamysis 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

Abbreviations: LC_{50}, median lethal concentration; LOEC, lowest observed effect concentration

[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 the original data were reported in mg/L.

[b] Values were estimated on the basis of the US EPA TRAP program.

7.1.4 Effects on sediment organisms

Although ecotoxicity data for thallium in sediments are 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 the chronic toxicity of thallium to *Hyalella* in tap water (from Lake Ontario) and in an artificial sediment without added potassium. The authors derived the lethal body concentration, resulting in 25% mortality (LBC_{25}) on the basis of 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 by 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 thallium accumulated by the organism from surrounding sediments was found to be 4.9 nmol/g (1.0 mg/kg), which was equivalent to approximately 2% of the 4-week LBC_{25}. This suggests that thallium levels of 0.53 nmol/g to 4.2 nmol/g (0.11 mg/kg to 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 on the 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) on the basis of reported thallium LOEC values for terrestrial plants and invertebrates (McCool 1933 as cited in CCME 1999; Lachover et al. 1958 as cited in CCME 1999; Environment Canada 1996, 1998 as cited in CCME 1999). The guideline value corresponds to the upper 98th percentile value of the range of typical thallium concentrations in Ontario soils (CCME 1999).

Heim et al. (2002) reported on the results of soil bioassay studies with plants and terrestrial invertebrates. For example, reproduction of terrestrial invertebrates is more sensitive to thallium in soils than are growth and mortality. Adverse effects on 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 earthworms represented more tolerant endpoints, with reported 4-week LOECs ranging from 100 mg/kg to 500 mg/kg. In the same study, the 7 d LOECs for garden cress (*Lepidium sativum*) seedlings were reported to be 10 mg/kg for shoot growth and 100 mg/kg for root growth.

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

Current information available for thallium soil toxicity indicates that a $PNEC_{soil}$ set at 1 mg/kg dw in soils, as per the 1999 CCME guideline, is protective for terrestrial organisms in the Canadian environment.

7.2 Ecological exposure assessment

7.2.1 Background concentrations

Thallium is ubiquitous in the environment, and in some areas of Canada, which are not impacted by anthropogenic activities (that is, 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 estimated by Kilgour & Associates Ltd. (2016). Using the approach from Kilgour & Associates Ltd. (2016), median background concentrations of thallium for Canadian ecozones were calculated from reference samples, deemed as such by the approach outlined in Proulx et al. (2018), collected from a variety of federal and provincial surface water quality monitoring programs and other repositories.[10] Median concentrations of thallium are also available for Lake Erie, Lake Ontario, Lake Huron, and Lake Superior using measurements taken between 2005 and 2015.[11] 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 µg/L to 0.05 µg/L (Table 7-3), which is similar to the freshwater thallium concentrations of 0.005 µg/L to 0.01 µg/L estimated by Reimann and de 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 increased concentrations of thallium. Median concentrations of thallium were also calculated for the Great Lakes (except Lake Michigan) using data collected from 2005 to 2015 by ECCC's Water Quality Monitoring and Surveillance group. Mean total dissolved concentrations of thallium (Table 7-3) ranged from 0.001 µg/L to 0.009 µg/L and were reasonably consistent with the values reported for the Great Lakes by Cheam (2001) and Cheam et al. (1995).

Table 7-3. Total thallium concentrations in surface waters 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

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[10] BQMA 2015; FQMS 2014; FQMS 2016; NLTWQM 2016; PWQMN [modified 2018]; 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.

[11] 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)
Boreal Plain	629 (51%)	<0.0003–4.4	0.05
Prairie	411 (88%)	<0.01–1.03	0.05
Taiga Cordillera	4 (NA)	0.002–0.066	0.006
Boreal Cordillera	286 (NA)	0.0005–0.164	0.003
Pacific Maritime	1322 (13%)	<0.001–0.239	0.002
Montane Cordillera	1336 (8.8%)	<0.001–0.058	0.003
Lake Superior	83 (93%)	0.0005–0.007 (DL 0.001)	0.001
Lake Superior[b]	NA	NA	0.001
Lake Huron	80 (100%)	0.002–0.013 (DL 0.001)	0.004
Lake Huron[b]	NA	NA	0.010
Lake Erie	106 (100%)	0.004–0.052 (DL 0.001)	0.009
Lake Erie[b]	NA	NA	0.009
Lake Ontario	165 (100%)	0.003–0.059 (DL 0.001)	0.007
Lake Ontario[b]	NA	NA	0.006
Lake Michigan[b]	NA	NA	0.014

Abbreviations: NA, not available

[a] Since total thallium concentrations were unavailable for the Atlantic Maritimes, dissolved thallium median concentrations were reported.

[b] Cheam 2001, unit converted from pmol/L.

Limited information is available for thallium concentrations in Canadian soils. OMEE (1993) reported 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 de Caritat (1998). A recent review also suggested that average background thallium concentrations range from 0.20 ppm to 0.82 ppm in soils around the world (Belzile and Chen 2017).

The natural content of thallium in plants was reported to be approximately 0.05 mg/kg by Krasnodebska-Ostrega and Golimowski (2008 as cited in Karbowska 2016) and less than 0.1 mg/kg dw by Geilmann et al. (1960 as cited in IPCS 1996). Thallium concentrations of 1 mg/kg were reported in plant ash (Dvornikov et al. 1973, 1976 as cited in IPCS 1996).

7.2.2 Approach for the exposure characterization

Detailed exposure scenarios were developed for the four sectoral activities that result in the highest releases of thallium to water, as determined from NPRI data (section 5). These exposure scenarios include releases of thallium from: 1) metal mining activities, 2) base metals smelting and refining, 3) coal-fired power generation facilities, and 4) wastewater treatment systems in Canada. Although not included in this assessment, exposure scenarios of thallium releases from other sectors (for example, pulp and paper, oil sands, and landfills) were also explored. The available data did not show any potential for ecological risk from the releases of thallium into surface water from these sectors at current levels of exposure.

PECs were primarily estimated using measured concentrations of thallium in surface water. Where both total and dissolved thallium concentrations were available, total thallium concentration was considered in the exposure analysis, given the greater availability of measurements and the ready water solubility as well as the very weak complexation tendency of Tl(I) with ligands in the aquatic environment. The adequacy of measured environmental concentrations was assessed by considering various factors such as the year and season of the sample collections, analytical method used and its detection limits, and the number of available measurements. Although they were determined from 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.

Where measured surface water concentrations were unavailable, estimated aquatic concentrations (EACs) were determined by applying a dilution factor of 10 to measured effluent concentrations. 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 EACs of thallium in the receiving environment (that is, PEC = EAC + median background concentration).

7.2.3 Metal mining

Thallium is a low-level constituent of many ores; it also coexists 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).

Air emissions from metal mining facilities were analyzed, and two distinct sources with different emissions profiles were observed. The iron ore pelletizing (IOP) process produces air emissions related to the use of induration furnaces, which differ from air emissions from traditional mining and ore concentration activities. The majority of thallium emitted to air originates from the induration process at pelletizing plants. NPRI data indicate that the IOP sector emitted 267 kg of thallium to air in 2020.

Beginning in 2018, IOP facilities in Canada were subject to air emissions requirements set out under an Environmental Performance Agreement signed that year under the initiatives of the Air Quality Management System (AQMS). The Agreement includes release limits for particulate matter (PM 2.5), which contain metals emitted to air, including thallium. Air emissions from IOP facilities are not considered further in this assessment. Instead, this current assessment focuses on releases of thallium to the aquatic environment as a result of effluent discharges.

For the years 2014 to 2020, total yearly releases of thallium and its compounds to water reported to the NPRI by the metal mining sector ranged from 6 kg to 55 kg (section 5 of this report) (NPRI 2021).

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*. Under the MDMER, thallium is required to be reported as part of the Environmental Effects Monitoring (EEM) provisions (EEM 2021). For determination of thallium in water and effluents under the amended MDMER, an analytical method detection limit (MDL) of 0.4 µg/L is in effect (Canada 2017b).

Thallium concentration data submitted through the MDMER (EEM 2021) as well as unpublished reports for 157 metal ore mining and milling sites that conducted EEM under the MDMER from 2004 to 2020 were reviewed. Measurements of thallium concentrations in effluent or in the receiving environment where effluent is discharged were available for 135 sites (approximately 86% of all sites), that is, 40 sites in the Ontario region, 33 sites in the Quebec region, 29 sites in the Northern-Prairie region, 17 sites in the Pacific region, and 16 sites in the Atlantic region (Canada 2021). On the basis of available data for effluent monitoring and monitoring of the exposure and reference areas,[12] 119 sites showed thallium concentrations of less than 0.4 µg/L (that is, the MDL for effluent concentration under the MDMER) in receiving water. Only 11 sites showed thallium concentrations equal to or greater than 0.4 µg/L from at least one detectable measurement in receiving water (Table 7-4). These 11 sites (8% of the 135 sites for which data were available) with moderate to high thallium concentrations (that is, ≥0.4 µg/L) detected in the receiving environment were further analyzed in this assessment report. Five sites had thallium concentrations that could not be interpreted because of limited measurements and high detection limits (MDL >0.8 µg/L).

Table 7-4. Summary of metal mining facilities that reported thallium concentrations in the receiving environment under the MDMER[a] (EEM 2021)

Number of metal mining sites (157 total)	Thallium concentration range at exposure areas
119 sites	<0.2 µg/L[b]–<0.4 µg/L in receiving waters
11 sites	≥0.4 µg/L in receiving waters
5 sites	Non-detectable with MDL >0.8 µg/L
22 sites	No data

Abbreviations: MDL, method detection limit

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[12] 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 fish habitat similar to that of the exposure area (see Schedule 5 of the MDMER).

[a] Including restricted, unpublished reports prepared for the Environmental Effects Monitoring provisions of the *Metal and Diamond Mining Effluent Regulations*.
[b] Concentrations below the MDL ranged from 0.002 µg/L to 0.2 µg/L.

Site-specific calculations for thallium concentrations were performed for 11 mining facilities or sites that showed concentrations of thallium equal to or greater than 0.4 µg/L in at least one measurement in the exposure areas. Metal mining facilities discharging effluent to the receiving environment between 2010 and 2020 were selected for the exposure analysis. Analytically non-detectable concentrations were substituted with the ½ MDL. Median and 75th percentile concentrations of thallium at Sites 1, 3, 5, 6, 7, and 11 were higher than those of the respective reference areas (Figure 7-2). Five facilities or sites (that is, Sites 2, 4, 8, 9, and 10) showed comparable detection frequencies (that is, detectable samples divided by sample size) and thallium concentrations between exposure and reference areas. The MDLs ranged from 0.002 µg/L to 5 µg/L.

Figure 7-2 presents the measured thallium concentrations in surface water at the exposure and reference areas of the 11 facilities or sites. Measurements for multiple reference or exposure areas are combined as one full data set for each site (for example, Sites 4, 6, 10, and 11).

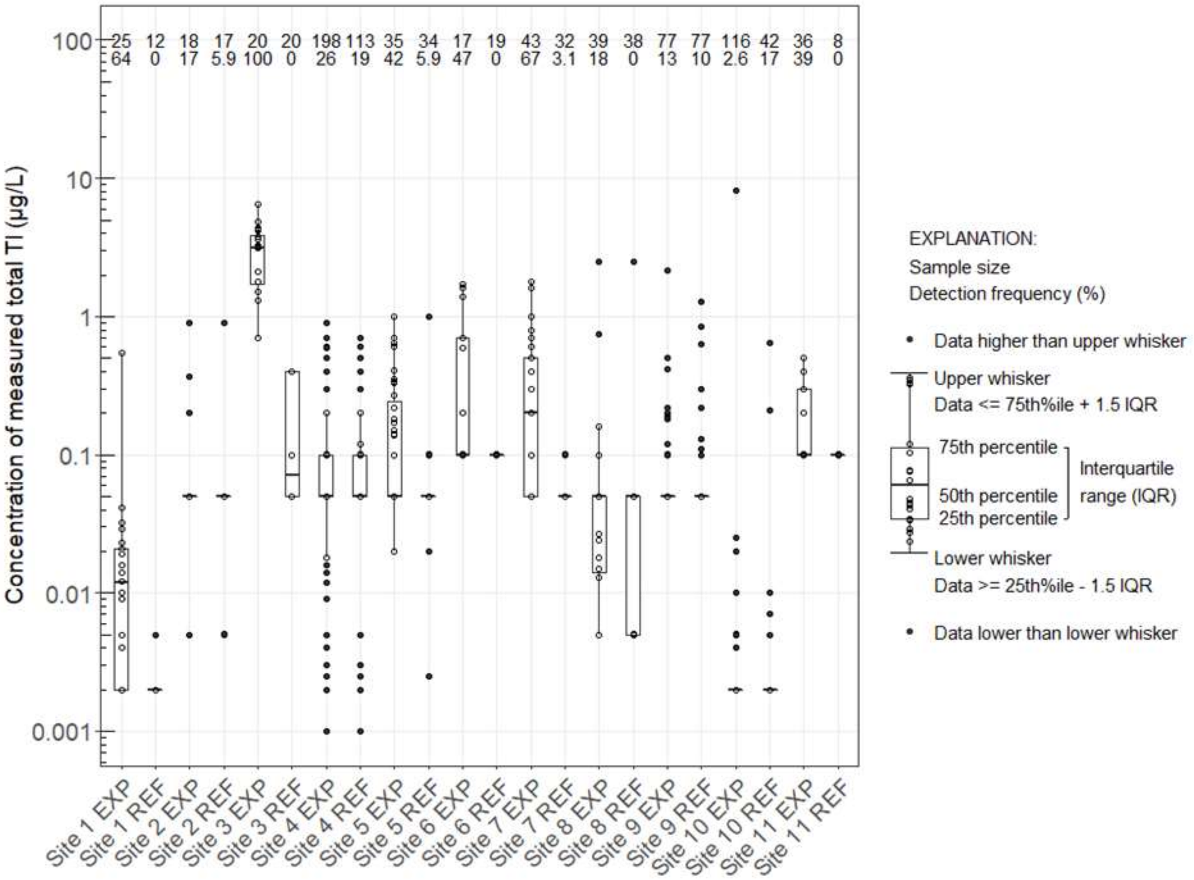

Figure 7-2. Box plots for thallium in surface water reported under the Environmental Effects Monitoring provisions of the MDMER for 11 metal mining sites (2010 to 2020)

[Long description: *Figure 7-2 uses box plots to summarize the thallium concentrations in surface water reported under the MDMER for the exposure and reference areas of 11 selected facilities or sites from 2010 to 2020 (EEM 2021). Thallium data were combined where multiple exposure and reference areas were available for Sites 4, 6, 10, and 11. Median and 75th percentile concentrations of thallium in the exposure areas at Sites 1, 3, 5, 6, 7, and 11 were higher than in the respective reference areas. Sites 6, 10, and 11 have multiple exposure and reference areas located on the same waterbodies, downstream and upstream, respectively, of the discharge point (for example, Site 6) or located on different waterbodies (for example, Sites 10 and 11). Site 4 has multiple metal mining facilities and discharge points with multiple exposure and reference areas located on the same waterbodies, downstream and upstream, respectively. The sample sizes, detection frequencies, and minimum, first quantile (25th percentile), 50th percentile, third quantile (75th percentile), 95th percentile, and maximum thallium concentrations are presented in the following table:*

Site[a] no.	**Sample size (n =)**	**Detection frequency (%)**	**Minimum (µg/L)**	**First quantile (µg/L)**	**50th percentile (µg/L)**	**Third quantile (µg/L)**	**95th percentile (µg/L)**	**Maximum (µg/L)**
Site 1 EXP	25	64	0.002[b]	0.002[b]	0.01	0.02	0.04	0.55
Site 1 REF	12	0	0.002[b]	0.002[b]	0.002[b]	0.002[b]	0.003[b]	0.005[b]
Site 2 EXP	18	17	0.005[b]	0.05[b]	0.05[b]	0.05[b]	0.45	0.9
Site 2 REF	17	5.9	0.005[b]	0.05[b]	0.05[b]	0.05[b]	0.22	0.9
Site 3[c] EXP	20	100	0.7	1.7	3.2	3.9	4.9	6.5
Site 3[c] REF	20	0	0.05[b]	0.05[b]	0.08[b]	0.4[b]	0.4[b]	0.4[b]
Site 4 EXP	198	26	0.001[b]	0.05[b]	0.05[b]	0.1[b]	0.4	0.9
Site 4 REF	113	19	0.001[b]	0.05[b]	0.05[b]	0.1[b]	0.4	0.7
Site 5 EXP	35	43	0.02[b]	0.05[b]	0.05[b]	0.24	0.66	1[b,d]
Site 5 REF	34	5.9	0.002[b]	0.05[b]	0.05[b]	0.05[b]	0.1	1[b,d]
Site 6 EXP	17	47	0.1[b]	0.1[b]	0.1[b]	0.7	1.6	1.7
Site 6 REF	19	0	0.1[b]	0.1[b]	0.1[b]	0.1[b]	0.1[b]	0.1[b]
Site 7 EXP	43	67	0.05[b]	0.05[b]	0.2	0.5	1.5	1.8
Site 7 REF	32	3.1	0.05[b]	0.05[b]	0.05[b]	0.05[b]	0.05[b]	0.1
Site 8 EXP	39	18	0.005[b]	0.01[b]	0.05[b]	0.05[b]	0.92	2.5[b,e]
Site 8 REF	38	0	0.005[b]	0.005[b]	0.05[b]	0.05[b]	0.42[b,e]	2.5[b,e]
Site 9 EXP	77	13	0.05[b]	0.05[b]	0.05[b]	0.05[b]	0.20	2.2
Site 9 REF	77	10	0.05[b]	0.05[b]	0.05[b]	0.05[b]	0.24	1.3
Site 10 EXP	116	2.6	0.002[b]	0.002[b]	0.002[b]	0.002[b]	0.006	8.2
Site 10 REF	42	17	0.002[b]	0.002[b]	0.002[b]	0.002[b]	0.2	0.65

Site 11 EXP	*36*	*39*	*0.1*[b]	*0.1*[b]	*0.1*[b]	*0.3*	*0.42*	*0.5*
Site 11 REF	*8*	*0*	*0.1*[b]	*0.1*[b]	*0.1*[b]	*0.1*[b]	*0.1*[b]	*0.1*[b]

Abbreviations: EXP, exposure area; REF, reference area; MDL, method detection limit of 0.002 µg/L to 5 µg/L

[a] *Exposure area means all fish habitat and waters frequented by fish that are exposed to effluent; reference area means waters frequented by fish that are not exposed to effluent and which have fish habitat that, as far as practicable, is most similar to that of the exposure area (Schedule 5 of the MDMER).*

[b] *Analytically non-detectable concentrations were substituted with the ½ MDL.*

[c] *The mining facility is closed; however, wastewater from mill process tailings and runoff is still being discharged post closure, albeit at reduced quantity. According to public comment by the stakeholder (2023), the discharge of effluent is expected to continue to decrease.*

[d] *One sample each for reference and exposure areas in 2019 with non-detectable concentrations at 2 µg/L were included in the statistics analysis. The highest detectable thallium concentration for the exposure areas was 0.7 µg/L. The highest detectable thallium concentration for the reference areas was 0.1 µg/L*

[e] *Two samples each for reference and exposure areas in 2013 with non-detectable concentrations at 5 µg/L were included in the statistics analysis. The highest detectable thallium concentration for the exposure areas was 0.74 µg/L. All thallium concentrations for the reference areas were below the MDL.*]

Data on thallium concentrations in effluents (Table 7-5), submitted through the MDMER, are available for 10 of the 11 mining facilities analyzed from 2019 to 2020 (EEM 2021). Thallium concentrations above 0.8 µg/L were detected (MDL of 0.004 µg/L to 2 µg/L) in effluents at Facilities 5, 7, and 11.

Table 7-5. Thallium concentrations in effluents reported in 2019 to 2020 for 11 metal mining sites under the MDMER (EEM 2021)

Facility number	Sample size (detectable)	Tl concentration range (µg/L)
1	7 (7)	0.026–0.051
2	5 (0)	<0.1[a]
3	NA	NA
4[b]	8 (8)	0.012–0.085[c]
5	8 (7)	0.15–1.83
6	8 (0)	<0.2[a]
7	8 (5)	<0.1[a]–1
8	9 (9)	0.014–0.04
9	8 (1)[d]	<0.1[a]–<1[a]
10	126 (21)[d]	<0.004[a]–<0.1[a]
11	7 (7)	0.3–3.1

Abbreviations: MDL, method detection limit of 0.004 µg/L to 2 µg/L; NA, not available

[a] Method detection limit

[b] Multiple metal mining facilities discharge effluents into the same watercourse. However, effluent concentration data are only available for one of the facilities.

[c] One sample of 22 000 µg/L was considered an outlier and excluded.

[d] Detectable effluent concentrations for thallium were below the highest MDL.

A divergence was observed in the thallium measurements for the effluent (Table 7-5) and exposure areas (Figure 7-2) of Facility 6. Although a detection frequency of 100% and thallium concentrations ranging from 0.6 µg/L to 1.7 µg/L at near- and mid-exposure areas were reported from 2011 to 2017 for this facility, concentrations at or below the MDL of 0.2 µg/L were reported in effluents and exposure areas from 2019 to 2020. This suggests that the discharge of thallium effluent from the facility has decreased in recent years.

In 2019, three additional metal mining facilities reported thallium effluent concentrations ranging from below the MDL (between 0.1 µg/L and 10 µg/L) to 0.2 µg/L via the NPRI (2021). The effluent concentrations or ½ MDL for non-detects were divided by a dilution factor of 10 to calculate the thallium EACs as described in section 7.2.2. The PEC for the receiving water was calculated as the sum of the EAC and the median background concentrations for the ecozone where the facility was located. The calculated PECs were as high as 0.55 µg/L.

7.2.4 Base metal smelting and refining (BMS)

There are currently 11 major base metals smelting and refining (BMS) facilities in Canada located in Alberta, British Columbia, Quebec, Manitoba, New Brunswick, Newfoundland and Labrador, and Ontario. The BMS sector processes concentrates from metal mines and mills as well as recycled materials (for example, electroplating, batteries) to purify, produce, and recover metals. Thallium is one of the residues or by-products produced during smelting processes. From 2014 to 2020, yearly releases of thallium and its compounds to water reported to the NPRI by BMS facilities ranged from 704 kg to 3067 kg, with average releases of 1769 kg ± 763 kg (standard deviation) (NPRI 2021). Annual releases to land, reported to the NPRI by the sector over the same period of 2014 to 2020, were negligible (NPRI 2021).

Releases from primary and secondary copper smelters and copper refineries as well as releases from primary and secondary zinc smelters and zinc refineries were assessed under the Second Priority Substances List (PSL2) Assessment Program (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 or refineries were listed on Schedule 1 of CEPA in 2003. BMS facilities in Canada were subsequently subject to air emissions requirements set out under the amended Pollution Prevention Planning notice published in the *Canada Gazette* in 2011 (Canada [modified 2011]). The Notice includes release limits for particulate matter, which contain most of the metals emitted to air, including thallium. Given these previous risk assessment and risk management activities, air emissions from BMS facilities are not considered further in this assessment. This current assessment instead focuses on releases of thallium to the aquatic environment as a result of effluent discharges.

Six BMS facilities that have combined effluents with metal mines submitted measurements of thallium concentrations in surface water and effluent as part of the EEM provisions under the MDMER (EEM 2021). BMS facilities that discharged effluent to the receiving environment during the 2010 to 2020 reporting period were selected for the exposure analysis. Thallium concentrations measured in surface water (data available for 2010 to 2020) and in effluent (data available for 2019 to 2020), submitted under the MDMER (EEM 2021) for Facilities 1 to 6, were pooled with thallium surface water data extracted from EEM reports for various reporting years and summarized in Table 7-6. Analytically non-detectable concentrations were substituted with the ½ MDL.

Measured thallium concentrations in effluents for Facilities 1 to 3 and Facility 5 ranged from below the MDLs (0.01 µg/L to 1 µg/L) to up to 0.4 µg/L (Table 7-6). Measured thallium concentrations in both the exposure and reference areas of these facilities were comparable (Table 7-6). These data suggest that the effluent released from these four facilities contributes a minimal addition of thallium to the receiving environment.

Median thallium concentrations in the exposure areas for Facilities 4 and 6 (Table 7-6) were 0.03 µg/L and 2 µg/L, respectively. This was higher than their reference area values (0.005 µg/L and 0.05 µg/L, respectively), suggesting that the effluent released from these two facilities contributes thallium to the receiving environment.

Table 7-6. Site-specific thallium concentrations in surface waters and effluents reported from 2010 to 2020 by base metal smelters and refineries under the MDMER

Facility number	Type of area[a]	Sample size (detectable)	Tl concentration range (µg/L)	Median[d] (µg/L)	95th percentile[d] (µg/L)
1	Exposure A+B[b]	81 (0)	0.01[c]–5[c]	0.05[c]	2.5[c]
1	Reference A+B[b]	76 (8)	0.01[c]–5[c]	0.05[c]	2.5[c]
1	Effluent	24 (0)	0.01[c]–0.1[c]	0.005[c]	0.01[c]
2	Exposure A+B[b]	50 (0)	0.01[c]–1[c]	0.05[c]	0.5[c]
2	Reference A+B[b]	40 (0)	0.1[c]–1[c]	0.05[c]	0.5[c]
2	Effluent	23 (19)	0.1[c]–0.4	0.1	0.3
3	Exposure	13 (0)	0.1[c]	0.05[c]	0.05[c]
3	Reference	16 (2)	0.1[c]	0.05[c]	0.1[c]
3	Effluent	10 (0)	0.1[c]	0.05[c]	0.05[c]
4	Exposure A+B[b]	32 (27)	0.0005[c]–0.2	0.03	0.1
4	Reference A+B+C[b]	25 (8)	0.0005[c]–0.045	0.005[c]	0.02[c]
4	Effluent	16 (16)	0.02–0.3	0.08	0.3
5	Exposure	16 (7)	0.0025[c]–0.1	0.05	0.1
5	Reference	11 (0)	0.0025[c]–0.05[c]	0.05[c]	0.05[c]
5	Effluent	4 (2)	0.0025[c]–0.09	0.04	0.09
6	Exposure	7 (3)	0.2[c]–10[c]	2	5[c,e]
6	Reference	7 (3)	0.2[c]–10[c]	0.5[c]	5[c,f]
6	Effluent	6 (3)	0.2[c]–11	3.4	9.3

[a] Exposure area refers to all fish habitat and waters frequented by fish that are exposed to effluent. Reference area refers to waters frequented by fish that are not exposed to effluent and which have fish habitat that, as far as practicable, is most similar to that of the exposure area (Schedule 5 of the MDMER).

[b] Data from facilities with multiple reference and exposure areas (identified as A, B, or C) are pooled.

[c] Method detection limit or statistics that are based on the ½ MDL.

[d] Analytically non-detectable concentrations were substituted with the ½ MDL.

[e] The highest detectable thallium concentration at the reference area was 1 µg/L (MDL at 0.2 µg/L).

[f] The highest detectable thallium concentration at the exposure area was 3.2 µg/L (MDL at 0.2 µg/L).

Thallium releases from two facilities (Facilities 7 and 8) that do not combine their effluent with metal mines were also analyzed. Thallium concentrations in receiving waters (exposure areas) and reference areas from 2011 to 2016 were available for Facility 7 (Table 7-7) (Ecoscape Environmental Consultants Ltd. and Larratt Aquatic Consulting Ltd. 2014, 2019). A total of 101 pairs of total and dissolved thallium surface water samples were collected from two reference sites (61% and 57% for total and dissolved detects, respectively, at a MDL of 0.002 µg/L to 0.2 µg/L), and 185 pairs of total and dissolved thallium surface water samples were collected from seven exposure sites (Discharge sites II, III, and IV and Exposure sites 2, 3, 4, and 5) from April 2011 to October 2016. Total thallium concentration data were used in the exposure analysis since dissolved and total concentrations were comparable (that is, a difference of -1% to 19%). Transect surface water samples were collected between 5 m and 35 m downstream of the three effluent discharge sites (Discharge sites II, III, and IV) during both low- and high-flow seasons in 2011. Three thallium samples collected in July 2011 from Discharge site III had concentrations of 0.62, 0.98, and 1.16 µg/L. Thallium concentrations were reduced to below 0.023 µg/L at the same location in November 2011. Discharge site III was the primary site receiving wastewater effluents from smelters and refineries of the facility (ChemInfo 2013) and is likely the site with the greatest releases of thallium. Thallium concentrations from Discharge sites II and IV were all below 0.4 µg/L during the same sampling periods (Table 7-7). Regular surface water samples were collected from two reference sites and four exposure sites (Table 7-7). Exposure site 2 is the initial dilution zone located 0.23 km downstream of the effluent Discharge site II and is estimated to be about 0.72 km downstream of Discharge site III. Samples collected at Exposure site 2 showed the highest median, third quantile, and 95th percentile thallium concentrations (Table 7-7). With the exception of Discharge site IV, median concentrations of thallium in surface water in all exposure areas are greater than in the reference areas.

Table 7-7. Concentrations of total thallium in reference areas and receiving environment from Smelter Facility 7 from 2011 to 2016 (Ecoscape Environmental Cconsultants Ltd. and Larratt Aquatic Consulting Ltd. 2014, 2019)

Type of area	Sample size (detect)	Concentration range (µg/L)	Median (µg/L)	Third quantile (µg/L)	95th percentile (µg/L)
Discharge site II[a]	6 (6)	0.028–0.40	0.13	0.22	0.36
Discharge site III[a]	6 (6)	0.0073–1.2	0.32	0.89	1.1
Discharge site IV[a]	6 (4)	<MDL–0.0023	0.0024	0.0024	0.0032
Exposure 2[b]	35 (31)	<MDL–1.6	0.25	0.50	0.91
Exposure 3[c]	35 (30)	<0.0092–0.20	0.065	0.10	0.13
Exposure 4[d]	14 (14)	0.009–0.054	0.019	0.026	0.038
Exposure 5[e]	83 (73)	0.0034–0.11	0.017	0.024	0.1[h]
Reference 1[f]	50 (32)	<MDL–<0.0082	0.0028	0.0034	0.1[h]
Reference 2[g]	51 (30)	<MDL–0.0087	0.0027	0.0035	0.1[h]

[a] Discharge sites II, III, and IV are the areas located between 5 m and 35 m downstream of the CII, CIII, and CIV outfalls.

[b] Exposure 2 is the initial dilution zone located approximately 0.23 km downstream of the CII outfall, approximately 0.72 km downstream of the CIII outfall. The right bank of Exposure area 2 is on the discharge plume path.

[c] Exposure 3 is located 1.09 km downstream of the CII outfall. The right bank of Exposure area 3 is on the discharge plume path.
[d] Exposure 4 is located 4.2 km downstream of the CII outfall. The right bank of Exposure area 4 is on the discharge plume path.
[e] Exposure 5 is the area located 15.8 km downstream of the CII outfall.
[f] Reference 1 is the area located 1.975 km upstream of the CII outfall.
[g] Reference 2 is the area located 9.72 km upstream of the CII outfall.
[h] MDL = method detection limit of 0.2 µg/L before May 2011 and 0.002 µg/L after July 2011.

Between 2016 and 2019, Facilities 7 and 8 reported annual thallium effluent concentrations ranging from 8.4 µg/L to 12.5 µg/L and 89 µg/L to 258 µg/L, respectively, to the NPRI (NPRI 2021). No report was submitted to the NPRI post-2019 for Facility 8 owing to closure of the facility. The thallium PECs were estimated from the annual effluent concentration as described in section 7.2.2. The calculated PECs ranged from 0.94 µg/L to 1.2 µg/L for Facility 7 and 89 µg/L to 258 µg/L for Facility 8.

7.2.5 Coal-fired electric power generation facilities

The volatilization of thallium from coal burning at high temperatures and subsequent re-condensation on finer ash particles can result in thallium concentrations on ash particles that are up to 10 times higher than in the coal itself (Cheam 2001). Therefore, effluent released from ash lagoons from the power generation sector has the potential to release thallium into the environment. Annual releases from facilities in this sector have been reported to the NPRI (see section 5); however, limited data are available for thallium concentrations near these facilities.

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, the technology developed also reduced overall particulate emissions to air, including co-existing heavy metal elements such as thallium. The *Reduction of Carbon Dioxide Emissions from Coal-Fired Generation of Electricity Regulations* (Canada 2022) is also expected to result in the phase-out of emissions from traditional coal-fired power plants, including other contaminants besides CO_2. The federal government’s intention to accelerate the phasing out of traditional coal-fired power plants by 2030 (Canada 2018) will, over time, further reduce the potential risk for other contaminants, including thallium.

Table 7-8 summarizes available measured thallium concentrations from effluents and receiving surface waters in the vicinity of 11 power generation facilities across Canada (Cheam et al. 2000; Cheam 2001; Alberta Environment 2006; NPRI 2021). Discharge from ash lagoons, leachate ponds, and wastewaters were considered effluents, and a dilution factor of 10 was applied to the concentrations of thallium in these effluents to calculate respective thallium EACs. The PEC was calculated as previously described (see section 7.2.2). The calculated PECs for 10 of the 11 power generation facilities were in the range of 0 µg/L to 0.56 µg/L. Calculated PECs in downstream discharges from an ash lagoon (Facility 7) decreased from 2.9 µg/L pre-2000 to approximately 0.1 µg/L (Table 7-8) between 2016 and 2019.

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 facilities 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 from the same lake in 2002 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 7-8).

Table 7-8. Thallium concentrations in effluents and receiving water in the vicinity of 11 power generation facilities across Canada

Facility number	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
3	2 km east of 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	Wastewater discharge to lagoon[b]	0.89	0.09	0.14
4	Effluent[e]	0.3–0.4	0.03–0.04	0.08–0.09
5	Ash leachate pond discharge[b]	0.40	0.04	0.09
5	Wastewater discharge[b]	0.56	0.06	0.10
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
7	Effluent[e]	0.3–0.48	0.03–0.05	0.08–0.10
8 & 9	Lake Wabamun[a]	0.01	0.01	0.01

Facility number	Location	Tl concentration[c] (µg/L)	EAC[c] (µg/L)	PEC[c,d] (µg/L)
10	Effluent[e]	0–0.1	0–0.01	0–0.06
11	Discharge into drainage ditch[a]	0.065	0.065	0.065

Abbreviations: EAC, estimated aquatic concentrations; PEC, predicted environmental concentrations

[a] The sites are considered on the basis of measured thallium concentration in the receiving water environment. No dilution factor or background concentrations were applied.

[b] Considered as effluent concentration; a dilution factor of 10 was applied to calculate the EAC.

[c] All values rounded up to 2 significant figures.

[d] PEC = EAC + median background concentration on the basis of ecozones where the facilities are located (Table 7-3).

[e] Effluent concentration for two discharge points for the facility, reported to the NPRI (2021) between 2016 and 2019.

7.2.6 Wastewater treatment systems

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). A Canadian wastewater treatment facility estimated releasing approximately 300 kg of thallium to water from 2014 to 2015 (NPRI 2021). Since most of the samples (94% in 2014 and 100% in 2015) had thallium concentrations that were below the MDLs, the estimates were derived as ½ MDLs. In 2016 and 2017, this facility removed thallium from their list of reportable substances as there had been “no results above the method detection limit (MDL) in two years” (personal communication, email from the Program Integration Division, Environment and Climate Change Canada (ECCC), to the Ecological Assessment Division, ECCC, dated January 29, 2018; unreferenced).

From 2009 to 2012, thallium releases were monitored at 25 wastewater treatment systems across Canada under the Chemicals Management Plan (CMP) Environmental Monitoring and Surveillance Program (Environment Canada 2013a). Final effluents were analyzed for total thallium concentrations in water. Thallium was quantitatively detected in only one (1) out of 191 (that is, 0.5%) samples at a concentration of 0.059 µg/L. In 2018 and 2019, effluent samples from 20 wastewater treatment systems were analyzed for both total and dissolved concentrations of thallium (Environment Canada 2019). The concentrations of total and dissolved thallium were in the range of below the MDL (0.01 µg/L) to 0.014 µg/L and below the MDL (0.001 µg/L) to 0.012 µg/L, respectively.

Although no direct releases to soils are anticipated, indirect releases may result from the application of Tl-containing biosolids (from wastewater treatment systems) to agricultural lands. In Canada, thallium is not regulated in biosolids, but its levels have declined significantly in recent decades, with median thallium concentrations in biosolids reported as being 0.26 mg/kg dw in 2009 compared to 16 mg/kg dw in 2001 (WEAO 2010). Similar low levels (in approximately 10% of samples) or quantitatively non-detectable levels were reported by 30 wastewater treatment systems across Canada from 2009 to 2019 (Environment Canada 2013a, 2019). A total of 112 primary sludge samples, 78 waste biological sludge samples, and 197 treated biosolids samples were analyzed for total thallium. Thallium was detected above the MDL of 0.001 mg/kg to 0.005 mg/kg in 99 of the 387 solids samples (that is, in 26% of samples), with maximal concentrations of 0.0168 mg/kg, 0.134 mg/kg, and 5.32 mg/kg in primary sludge, waste biological sludge, and treated biosolids samples, respectively. Biosolids from wastewater treatment systems are sent to landfills, incinerated, or used for land applications. The equation below was used to estimate the input of thallium to soils through the land application of biosolids.

$$\mathrm{PEC} = \frac{\text{Total Tl concentration in biosolids} \times \text{application rate} \times \text{number of years}}{\text{mixing depth} \times \text{soil density}}$$

To calculate a conservative exposure scenario for soil-dwelling organisms, a maximum biosolids application rate of 0.83 kg/m^2 dw per year (on the basis of the highest existing provincial regulatory limit; Environment Canada 2006), a mixing depth of 0.2 m (plough depth; ECHA 2012), and a soil density of 1200 kg/m^3 (Williams 1991) were input into the above equation, along with the highest concentration of thallium measured in biosolids from wastewater treatment systems in Canada that are not destined for incineration. A period of 10 consecutive years was chosen as the duration of application (ECHA 2012). The cumulative thallium concentration in soil at the end of this period is 0.18 mg/kg for the highest concentration sampled in biosolids.

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

Data from the CMP monitoring program and the NPRI suggest that annual thallium releases to water or soils from wastewater treatment systems are insignificant.

7.3 Characterization of ecological risk

The approach taken in this ecological assessment was to examine the assessment information and develop conclusions using a weight of evidence approach and precaution. 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 evaluated in this assessment that support the characterization of ecological risk in the Canadian environment. Reliable secondary or indirect lines of evidence are considered when available, including classifications of hazard or fate characteristics made by other regulatory agencies. The potential for cumulative effects was considered in this assessment by examining cumulative exposures to the moiety of thallium.

7.3.1 Risk quotient analysis

Risk quotient (RQ) analyses were performed by comparing estimates of exposure (PECs; see the Ecological Exposure Assessment under section 7.2 of this report) with ecological toxicity information (PNECs; see 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 (that is, surface fresh waters or marine waters) in the exposure scenarios described in section 7.2 for four sectors: metal mining, base metals smelting, coal-fired power generation stations, and wastewater systems.

The ecological risk characterization for the metal mining sector utilized effluent and surface fresh water data submitted under the EEM provisions of the MDMER for the period of 2010 to 2020 (EEM 2021) as well as annual effluent concentration data reported to the NPRI for three additional facilities (NPRI 2021). The PECs therefore consisted primarily of thallium concentrations measured in the receiving environments (that is, exposure areas) and corresponding reference areas of metal mining facilities. RQs were calculated for 11 metal mining facilities identified for ecological exposure assessment in section 7.2.3 of this report. Box plots (Figure 7-3) generated for the 11 facilities display the distribution of RQs, with a red line to indicate where the RQ is equal to 1.

The results of the RQ calculations indicate potential for ecological risk at Site 3. At Site 3, thallium was detected in all samples collected in the exposure area from 2011 to 2016, whereas thallium was not detected in the reference area. In total, 85% of the measurements exceeded the $\text{PNEC}_{\text{water}}$, with a median thallium concentration of 3.2 µg/L, which is equivalent to a RQ of 4.0. Although Facility 3 has ceased to operate, wastewater from its mill process, tailings, and runoffs was still being discharged post closure, albeit at reduced quantity. Median thallium concentrations decreased from a range of 3.7 µg/L to 4.0 µg/L and 100% $\text{PNEC}_{\text{water}}$ exceedance during operation to 3.2 µg/L, 1.7 µg/L, and 1.6 µg/L in consecutive years and 75% $\text{PNEC}_{\text{water}}$ exceedance post closure. These measurements indicate continuing potential for ecological harm; however, thallium measurements more recent than 2016 are not available.

The near-exposure area of Site 6 exhibited elevated thallium concentrations, with a median concentration of 1.6 µg/L, and all three measurements between 2011 and 2017 exceeded the $\text{PNEC}_{\text{water}}$ (0.8 µg/L). From 2019 to 2020, thallium concentrations decreased to equal to or less than 0.2 µg/L at the exposure area (and in effluent concentrations) of the Site 6 facility, suggesting reduced ecological harm at Facility 6 in recent years. Thallium concentrations in approximately 45% of samples collected in the exposure area for Site 7 were between 0.4 µg/L and 1.8 µg/L; only the 95th percentile concentration (1.5 µg/L) for the site was above the $\text{PNEC}_{\text{water}}$, whereas both the median and third quantile concentrations (that is, 0.2 µg/L and 0.5 µg/L, respectively) were below the $\text{PNEC}_{\text{water}}$. High detection frequency at RQs of between 0.5 to 2.2 at the exposure area may indicate potential for concern at this facility.

Occasional PNEC_{water} exceedances were observed at other sites analyzed, which may be non-detectable. For example, Site 5 had one sample each for reference and exposure areas in 2019 with non-detectable concentrations at 2 µg/L, while the highest detectable thallium concentrations were 0.7 µg/L and 0.1 µg/L at the exposure area and reference area, respectively. Site 8 had two samples each for reference and exposure areas in 2013 with non-detectable concentrations at 5 µg/L, while the highest detectable thallium concentrations were 0.74 µg/L and below the MDL (0.01 µg/L to 0.1 µg/L) at the exposure and reference areas, respectively. Occasional PNEC_{water} exceedances at other sites were considered transient (for example, Sites 2 and 10) when all other measurements were below 0.8 µg/L.

The calculated PECs for three additional metal mining facilities that reported thallium effluent concentrations via the NPRI (2021) were less than 0.55 µg/L, equivalent to RQs below 0.69 (data not shown in Figure 7-3).

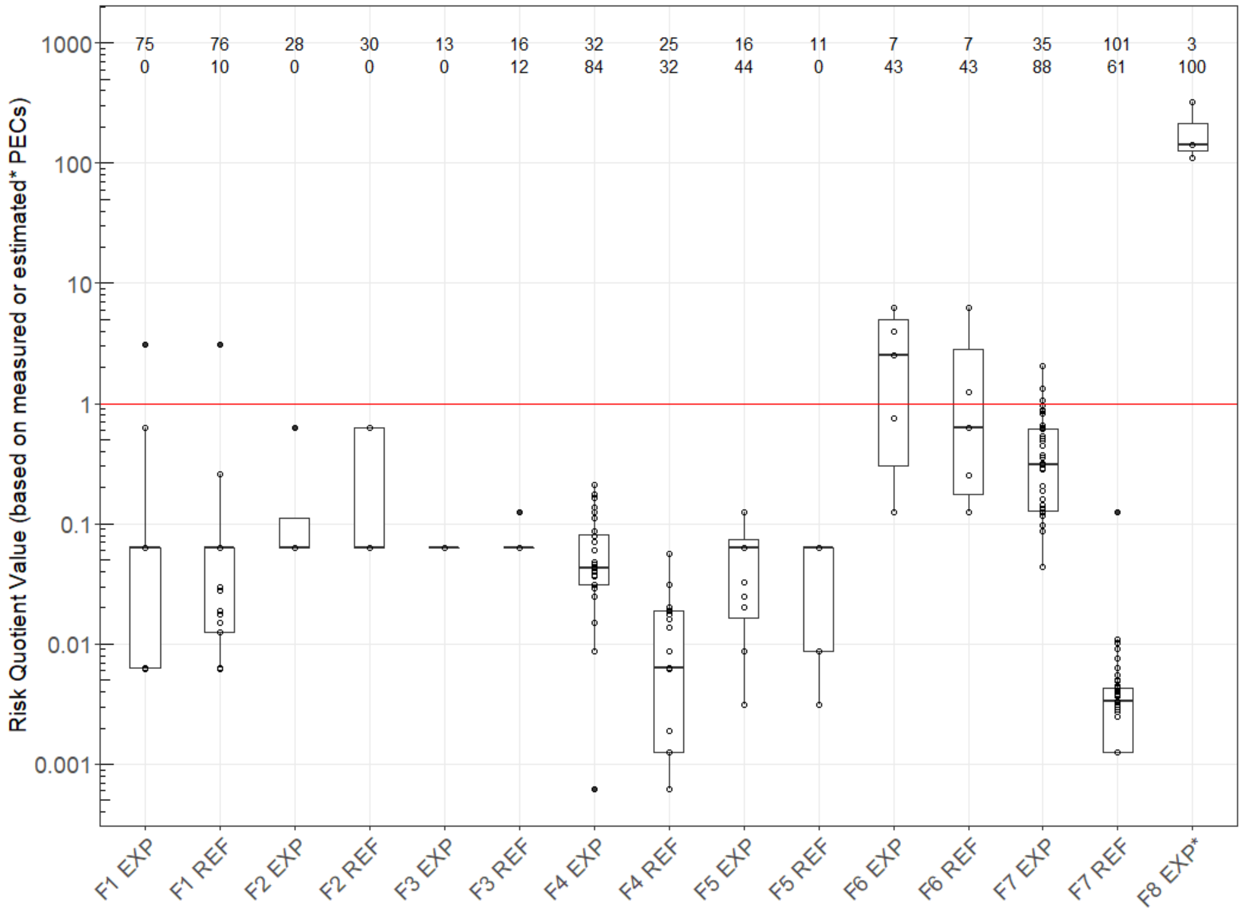

Figure 7-3. Box plots of risk quotients (the red line represents a $\mathrm{PNEC}_{\mathrm{water}}$ of 0.8 µg/L relative to thallium concentrations measured, equivalent to a RQ of 1) on the basis of thallium concentrations for 11 metal mining sites from 2010 to 2020 (EEM 2021)

See Figure 7-2 for an explanation of the data presented in the box plots.

***[Long description:** Figure 7-3 uses box plots to summarize thallium concentrations in surface water for the exposure and reference areas of 11 selected sites reported under the MDMER from 2010 to 2020 (EEM 2021). Thallium data were combined where multiple exposure and reference areas are available for Sites 4, 6, 10, and 11.*

The sample sizes, detection frequencies, minimum RQ, median RQ, 95th RQ, and maximum RQ are shown in the following table:

Site[a] number	***Sample size***	***Detection frequency (%)***	***Minimum RQ***	***Median RQ***	***95th RQ***	***Max RQ***
Site 1 EXP	*25*	*64*	*0.002*	*0.02*	*0.05*	*0.9*
Site 1 REF	*12*	*0*	*0.002*	*0.002*	*0.004*	*0.006*
Site 2 EXP	*18*	*17*	*0.006*	*0.06*	*0.6*	*1.1*
Site 2 REF	*17*	*5.9*	*0.006*	*0.06*	*0.3*	*1.1*
Site 3[b] EXP	*20*	*100*	*0.9*	*3.9*	*6.1*	*8.1*
Site 3[b] REF	*20*	*0*	*0.06*	*0.09*	*0.5*	*0.5*
Site 4 EXP	*198*	*26*	*0.001*	*0.06*	*0.5*	*1.1*
Site 4 REF	*113*	*19*	*0.001*	*0.06*	*0.5*	*0.9*
Site 5 EXP	*35*	*43*	*0.02*	*0.06*	*0.8[c]*	*1.2[c]*
Site 5 REF	*34*	*5.9*	*0.003*	*0.06*	*0.1[c]*	*1.2[c]*
Site 6 EXP	*17*	*47*	*0.1*	*0.212*	*2.0*	*2.1*
Site 6 REF	*19*	*0*	*0.1*	*0.1*	*0.1*	*0.1*
Site 7 EXP	*43*	*67*	*0.06*	*0.2*	*1.9*	*2.2*
Site 7 REF	*32*	*3.1*	*0.06*	*0.06*	*0.06*	*0.1*
Site 8 EXP	*39*	*18*	*0.006*	*0.06*	*1.1[d]*	*3.1[d]*
Site 8 REF	*38*	*0*	*0.006*	*0.06*	*0.5[d]*	*3.1[d]*
Site 9 EXP	*77*	*13*	*0.06*	*0.06*	*0.2*	*2.7*
Site 9 REF	*77*	*10*	*0.06*	*0.06*	*0.3*	*1.6*
Site 10 EXP	*116*	*2.6*	*0.002*	*0.002*	*0.008*	*10*
Site 10 REF	*42*	*17*	*0.002*	*0.002*	*0.2*	*0.8*
Site 11 EXP	*36*	*39*	*0.1*	*0.1*	*0.5*	*0.6*
Site 11 REF	*8*	*0*	*0.1*	*0.1*	*0.1*	*0.1*

Abbreviations: EXP, exposure area; REF, reference area; RQ risk quotient

[a] Exposure area means all fish habitat and waters frequented by fish that are exposed to effluent; reference area means water frequented by fish that are not exposed to effluent and which have fish habitat that, as far as practicable, is most similar to that of the exposure area (Schedule 5 of the MDMER).

[b] The mining facility is closed; however, wastewater from mill process tailings and runoffs was still being discharged post closure, albeit at reduced quantity. According to public comment by the stakeholder (2023), the discharge of effluent is expected to continue to decrease.

[c] One measurement each for reference and exposure areas in 2019 with non-detectable concentrations at 2 µg/L was included in the statistical analysis. The highest detectable thallium concentration at the exposure area was 0.7 µg/L. The highest detectable thallium concentration at the reference area was 0.1 µg/L.

*[d] Two measurements each for reference and exposure areas in 2013 with non-detectable concentrations at 5 µg/L were included in the statistics analysis. The highest detectable thallium concentration at the exposure area was 0.74 µg/L. All thallium concentrations at the reference area were below the MDL.***]**

The ecological risk characterization for the base metals smelting sector utilized surface fresh and marine water data or effluent data submitted under the EEM provisions of the MDMER between 2010 and 2020 for the six facilities that combine their effluents with metal mines (EEM 2021). Data reported to the NPRI for two stand-alone facilities (NPRI 2021) and data from an environmental assessment report for one of these facilities (Ecoscape Environmental Consultants Ltd. and Larratt Aquatic Consulting Ltd. 2014, 2019) were also utilized. Box plots (Figure 7-4) generated for the eight facilities display the distribution of RQs, with a red line to indicate where the RQ is equal to 1. Five facilities that combine their effluents with metal mines (Facilities 1 to 5) showed low RQs and are considered unlikely to pose ecological harm. Data for Facilities 6 and 8 indicated exceedances of the $PNEC_{water}$ (RQs 2.5 to 320). Facility 6 showed high median concentrations of thallium at the exposure area in exceedance of the $PNEC_{water}$ (that is, two pairs of thallium concentrations for both reference and exposure areas in exceedance of the $PNEC_{water}$ were non-detect measurements and excluded from RQ calculation). The highest detectable measurements were 3.2 µg/L and 1 µg/L at the exposure and reference areas, respectively. Facility 7 has multiple discharge points and exposure areas. Exposure area 2 (located approximately 0.72 km downstream of Discharge site III) showed that 34% of measurements had RQs between 0.5 and 2.0, which suggests some level of concern from releases of thallium. High thallium concentrations detected near Discharge site III, which is located between 5 m and 35 m from the effluent outfall, also suggest that exposure areas in the vicinity of this discharge site may be of potential concern for thallium. To provide a further line of evidence, the predicted environmental thallium concentration was also estimated from the yearly effluent concentrations reported to the NPRI by the facility from 2016 to 2019 (NPRI 2021). The calculated PECs ranged from 0.89 µg/L to 1.2 µg/L, equivalent to RQs of 1.0 to 1.5, suggesting further evidence of potential concern from thallium releases at this facility.

Facility 8 reported annual effluent concentrations from 2016 to 2018 to the NPRI (NPRI 2021). No report was submitted to the NPRI post-2019 owing to the closure of the facility. The thallium PECs were estimated from the yearly effluent concentration as described in Section 7.2.2. The calculated PECs were from 89 to 258 µg/L, which is significantly higher than the $PNEC_{water}$ of 0.8 µg/L, equivalent to RQs of 110 to 320.

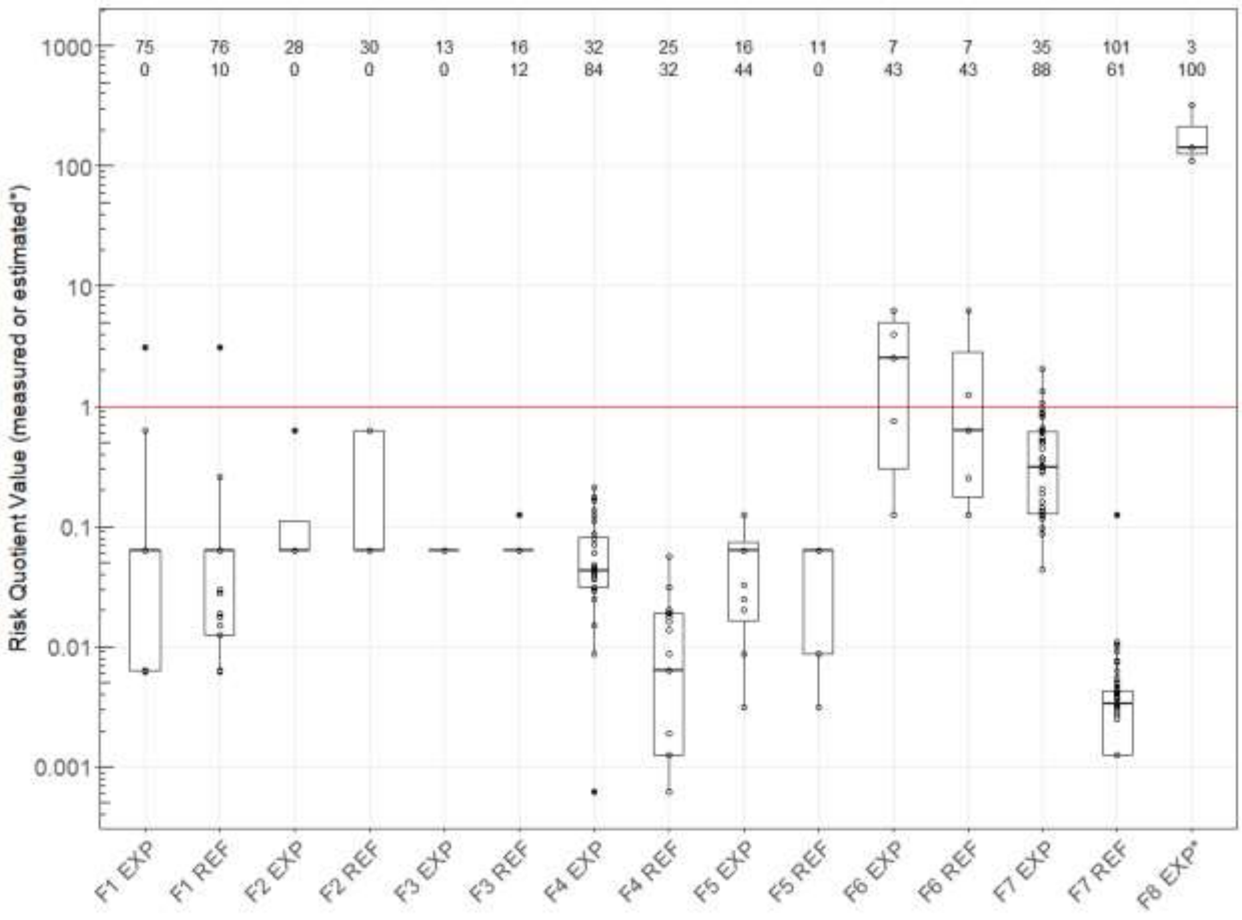

Figure 7-4. Box plots of risk quotients (the red line represents a PNEC$_{water}$ of 0.8 µg/L relative to thallium concentrations measured, equivalent to a RQ of 1) on the basis of measured thallium concentrations for 7 base metal smelting facilities from 2010 to 2020 (EEM 2021) and estimated thallium concentrations for 1 base metal smelting facility* from 2016 to 2018 (NPRI 2021)

See Figure 7-2 for an explanation of the data presented in the box plots.

***[Long description:** Figure 7-4 uses box plots to summarize the thallium risk quotients for the exposure and reference areas of 7 selected facilities reported under the MDMER from 2010 to 2020 (EEM 2021) as well as the risk quotients calculated on the basis of estimated PECs for Facility 8 EXP* from 2016 to 2018 (NPRI 2021). Thallium data were combined where multiple exposure and reference areas were available for Facilities 1, 2, 4, and 7. Facility 6 showed high median concentrations of thallium at the exposure area in exceedance of the PNEC$_{water}$. For Facility 7, thallium concentrations at the exposure area were higher than at the reference area; however, only the 95th percentile concentration for Exposure area 2 (all four exposure areas for the facility are in the same water stream, and only the near-exposure area of the facility is included in the box plot) exceeds the PNEC$_{water}$. Since the RQ values for Facility 8 were calculated from* *estimated PECs, no data for a reference area at the facility are available. The sample sizes, detection frequencies, minimum RQ, median RQ, 95th percentile RQ, and maximum RQ are shown in the following table:*

Facility[a] number	*Sample size*	*Detection frequency (%)*	*Minimum RQ*	*Median RQ*	*95th RQ*	*Max. RQ*
F1 EXP	*75*	*0*	*0.0062*	*0.062*	*3.1[b]*	*3.1[b]*
F1 REF	*76*	*10*	*0.0062*	*0.062*	*3.1[b]*	*3.1[b]*
F2 EXP	*28*	*0*	*0.062*	*0.062*	*0.62*	*0.62*
F2 REF	*30*	*0*	*0.062*	*0.062*	*0.62*	*0.62*
F3 EXP	*13*	*0*	*0.062*	*0.062*	*0.062*	*0.062*
F3 REF	*16*	*12*	*0.062*	*0.062*	*0.12*	*0.12*
F4 EXP	*32*	*84*	*0.00062*	*0.042*	*0.17*	*0.21*
F4 REF	*25*	*32*	*0.00062*	*0.0062*	*0.031*	*0.056*
F5 EXP	*16*	*44*	*0.0031*	*0.062*	*0.12*	*0.12*
F5 REF	*11*	*0*	*0.0031*	*0.062*	*0.062*	*0.062*
F6 EXP[c]	*7*	*43*	*0.12*	*2.5*	*6.2[c]*	*6.2[c]*
F6 REF[c]	*7*	*43*	*0.12*	*0.62*	*6.2[c]*	*6.2[c]*
F7 EXP	*35*	*88*	*0.044*	*0.37*	*1.1*	*2.0*
F7 REF	*101*	*61*	*0.0012*	*0.0034*	*0.12*	*0.12*
F8 EXP[d]	*3*	*100*	*111*	*142*	*304*	*322*

Abbreviations: EXP, exposure area; REF, reference area; RQ, risk quotient

[a] Exposure area means all fish habitat and waters frequented by fish that are exposed to effluent; reference area means water frequented by fish that are not exposed to effluent and which have fish habitat that, as far as practicable, is most similar to that of the exposure area (Schedule 5 of the MDMER).

[b] The highest measurements for both reference and exposure areas with non-detectable concentrations of 5 µg/L were included in the statistical analysis. All measurements at the exposure area were below the MDL of 0.01 µg/L to 5 µg/L.

[c] Two pairs of the highest measurements each for reference and exposure areas in 2019 and 2020 with non-detectable concentrations of 10 µg/L ertr included in the statistical analysis. The highest detectable thallium concentration at the exposure area was 3.2 µg/L. The highest detectable thallium concentration at the reference area was 1 µg/L

[d] Surface water data were not available for Facility 8. The RQ value of the facility was calculated from PECs estimated on the basis of thallium effluent concentrations from 2016 to 2018 (NPRI 2021).]

The ecological risk characterization for the coal-fired power-generating sector utilized fresh water data published by Cheam (2001), effluent concentrations reported to the NPRI (2021), and the results of the water quality surveys of Wabamun Lake (Alberta Environment 2006). The PECs include measured data for thallium in surface fresh water downstream of the discharge sites of the power generation facilities. Alternatively, PECs were calculated by applying a dilution factor of 10 to the concentrations of thallium in the effluents of wastewater discharging sites and adding the appropriate median background concentration of total thallium in surface water. On the basis of data from Cheam et al. (2000) and Cheam (2001), one facility showed potential for ecological concern owing to releases of thallium at the discharge point of its ash lagoon, with a RQ of 3.6 (PEC of 2.9 µg/L). However, more recently in 2018 and 2019, the facility reported thallium effluent concentrations of 0.3 µg/L to 0.48 µg/L, with a RQ of approximately 0.1 (NPRI 2021). In addition to low 6-year annual water release quantities reported to the NPRI by the sector, the latest available exposure data suggest that effluents discharged to surface fresh water from coal-fired power generation facilities are not likely to pose an ecological concern.

The ecological risk characterization for wastewater treatment systems in Canada utilized effluent and biosolids data collected under the CMP Environmental Monitoring and Surveillance Program (Environment Canada 2013a, 2019). The PECs were calculated by applying a dilution factor of 10 to the concentrations of thallium in the effluents of wastewater discharging sites and adding the appropriate median background concentration of total thallium in surface water. The RQs are between 0.003 and 0.06, suggesting that effluents discharged from wastewater treatment systems are not likely to pose an ecological concern. The highest cumulative thallium concentration calculated for soil is 0.18 mg/kg, equivalent to a RQ of 0.18 (that is, $\text{PNEC}_{\text{soil}}$ of 1 mg/kg), which also suggests that applying biosolids from wastewater treatment systems to agricultural lands are not likely to pose an ecological concern.

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 7-9, 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 7-9. Weighted lines of key evidence considered in order 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	High
PNEC for organisms in soil	Moderate	Moderate	Moderate

Line of evidence	Level of confidence [a]	Relevance in assessment[b]	Weight assigned[c]
Monitoring data for concentrations of thallium in surface water (PECs for metal mining)	High	High	High
Monitoring data for concentrations of thallium in surface water (PECs for base metal smelting)	Moderate	High	Moderate–high
Monitoring data for concentrations of thallium in surface water and effluent (PECs for coal-fired power generation)	Moderate	High	Moderate–high
Estimated data for concentrations of thallium in surface water and soils (wastewater systems)	Moderate	High	Moderate–high
RQ(s) for metal mining facilities	High	High	High
RQ(s) for base metal smelting facilities	Moderate	High	Moderate-high
RQ(s) for electric power generation facilities	Moderate	High	Moderate-high
RQ(s) for wastewater treatment system	Moderate	High	Moderate–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 whether 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 accumulates in aquatic and soil-dwelling organisms and, particularly, plants. Although thallium may not appear to bioaccumulate in organisms, considerably elevated thallium concentrations in organisms near sources of release (for example, smelters) have been reported. However, thallium's biomagnification potential in ecosystems is uncertain owing to conflicting information.

Thallium has two oxidation states, Tl(I) and Tl(III), and its speciation in surface water 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 and uptake of thallium in organisms is, however, dependent upon thallium 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 $\text{PNEC}_{\text{water}}$.

Thallium is released to the aquatic compartment from many industries, including metal mining, base metals smelting, coal-fired power generation facilities, and wastewater treatment systems in Canada. For most facilities, releases are limited and unlikely to pose ecological risk, but a small number of facilities from metal mining and base metals smelting sectors may release thallium to a degree that is of ecological concern.

In the metal mining sector in Canada, information on thallium concentrations in receiving surface waters or in effluents is available for 160 facilities, approximately 86% of metal mining sites in operation during 2004 and 2020 (EEM 2021; NPRI 2021). The exposure analysis focused on facilities with at least one measurement equal to or above 0.4 µg/L (that is, one-half of the $\text{PNEC}_{\text{water}}$) between 2010 and 2020. Of the 11 facilities that met this criterion, releases of thallium at one facility (that is, Site 3; Figure 7-3) showed the clearest potential for ecological concern. Median thallium concentrations at this site were higher than the $\text{PNEC}_{\text{water}}$ and the risk quotients ranged from 0.9 to 8.1. Risk quotients in the corresponding reference area were all below 1 (0.06 to 0.5). This site has currently ceased operations; however, wastewater from its mill process tailings and runoffs was still being discharged post operation. During those years, thallium concentrations at the exposure area exceeded the $\text{PNEC}_{\text{water}}$ in 75% of the samples. In addition to Site 3, the available data also suggest potential for ecological concern at Sites 6 and 7; however, the strength of evidence is less clear for these facilities. For Site 6, all measurements at the near-exposure area prior to 2018 exceeded the $\text{PNEC}_{\text{water}}$, while data from 2018 and 2019 (EEM 2021) for the exposure area and in effluents were all below the $\text{PNEC}_{\text{water}}$, suggesting a reduction in discharges from the facility in recent years. At Site 7, thallium was detected in the exposure area in approximately half (that is, 45%) of the measurements, with RQs ranging from 0.5 to 2.2. While this indicates potential for concern, only 9.5% of samples exceeded the $\text{PNEC}_{\text{water}}$, which suggests that the potential for ecological harm at this site is inconsistent.

Five BMS facilities that combine effluents with metal mines showed low potential for ecological concern. However, one BMS facility that combines effluents with metal mines

(Facility 6) and one stand-alone BMS facility (Facility 8) release effluents containing thallium that result in environmental concentrations higher than the $PNEC_{water}$, with maximum risk quotients of 2.5 and 320, respectively. Although Facility 8 was recently closed, high $PNEC_{water}$ exceedance (based on information available up until 2018) suggest that the environmental releases from the facility could continue post operation. Facility 7 also showed potential for ecological concern as the thallium detection frequency was high, and one-third of measurements had RQs from 0.5 to 2 at the exposure area nearest one of the discharging sites in addition to a marginal PNEC exceedance with calculated RQs from 1.1 to 1.6 at a near-field discharge point.

One (out of the 11) coal-fired power generation facilities was releasing thallium into water that resulted in concentrations higher than the $PNEC_{water}$, with a maximum RQ greater than 3, according to discharge data collected before the year 2000 (Cheam 2000, 2001). The same facility submitted effluent concentration data to the NPRI (2021) in 2018 and 2019 and calculated RQs for both years were at 0.1. Considering the low quantity (from 0 kg to less than 1 kg per year) of thallium releases to water reported by the sector to the NPRI between 2014 and 2019 and the low RQs on the basis of the most recent data, thallium effluent discharge by coal-fired power generation facilities may be considered unlikely to be causing ecological harm.

Thallium uses (section 4.3) and NPRI data (section 5) suggest that wastewater treatment systems may release thallium into the environment. However, further data submitted to the NPRI as well as information from the CMP Environmental Monitoring and Surveillance Program (Environment Canada 2013a, 2019) indicate that thallium releases to water from these facilities and the application of biosolids to agriculture lands are of low ecological 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 four sectors: metal mining, base metals smelting and refining, coal-fired electric power generation stations, and wastewater treatment systems.

The risk characterization of thallium in the metal mining sector in Canada for mining Site 3 used available data on thallium concentrations in the receiving surface water from up to 2016. It was recognized that mining Site 3 has ceased to operate and that the median thallium concentrations in receiving water post-operation decreased by approximately half. However, RQs remain elevated. Data that are more recent may show a further reduction in concentrations and RQs. Five metal mining facilities (Table 7-4) reported non-detectable thallium concentrations in the exposure areas at a MDL above the $PNEC_{water}$ (for example, 1 µg/L to 2 µg/L). Samples from mining sites with a MDL greater than the $PNEC_{water}$ value (that is, one pair of reference and exposure samples for mining Site 5 in 2019 and two pairs of reference and exposure samples for mining

Site 8 in 2013) were included in the analysis, which may cause bias in the statistical analysis (that is, non-detectable values were greater than the $\text{PNEC}_{\text{water}}$ value and represented the maximum value for both sites). However, this uncertainty does not affect the interpretation of anthropogenic releases of thallium from facilities of the sector.

The risk characterization of thallium in the base metals smelting sector was limited to eight facilities where exposure data were available for surface water or effluent. BMS Facility 7 reported measured thallium concentrations from seven discharge and exposure sites, the majority of which had RQs of less than 1. However, the data suggest that thallium was predominantly released from Discharge site III and the nearest exposure area (Exposure area 2), where approximately one-third of the measurements had RQs of above 0.5, with some $\text{PNEC}_{\text{water}}$ exceedances. The PECs for thus facility were calculated from effluent concentrations (NPRI 2021) to further assess the level of potential concern nearest to Discharge site III. The resulting RQs of between 1.1 and 1.6 served as an additional line of evidence suggesting some concern in the vicinity of this discharge site. Samples from Facility 6 with non-detectable values greater than the $\text{PNEC}_{\text{water}}$ value and that represented the maximum value (that is, two pairs of reference and exposure samples) were also included in the box plot (Figure 7-4), which may cause bias in the statistical analysis. However, this uncertainty does not affect the RQ calculation and interpretation of anthropogenic releases of thallium from the facility. Owing to the lack of data for surface water, the PECs for Facility 8 were estimated from annual effluent concentrations reported to the NPRI (2021). Additionally, site-specific data from receiving surface water could avoid the uncertainty of needing to incorporate a dilution factor or a representative background concentration into the PEC calculation. The impact of this uncertainty on the assessment’s conclusion cannot be determined. The recent closure of BMS Facility 8 may result in a reduction in effluent discharged from the facility; however, discharges of concern may still occur post closure, as in the case of mining Facility 3.

Some data sets of measured environmental concentrations contained non-detects and these were replaced with one-half of the reported MDL. A sensitivity analysis was conducted to determine if the replacement choice (½ MDL) produced false positives in the ecological risk outcome. However, replacement with 0 yielded similar results.

Exposure and reference areas may be located downstream and upstream on the same waterbody, or they may be located on different waterbodies (that is, not necessarily paired upstream and downstream). It appears that, in some cases, some metal concentrations in the reference area may be influenced by natural or anthropogenic factors, resulting in higher values than in the designated exposure area. However, this confounding factor was not significant enough to influence the weight of evidence in the risk characterization.

Given the consistent availability of total measurements, measurements of total thallium concentrations were preferred over dissolved thallium concentrations when both sets of data were available in the environmental exposure analysis. Although this is a potentially conservative approach, it was recognized that Tl(I) is readily soluble and has a very weak complexation tendency with ligands in surface water. Furthermore, total thallium concentrations were often close (80% to 100%) to dissolved thallium concentrations when both sets of data were available. A recent study by Nagel et al. (2019), which systematically assessed the effect of water chemistry on thallium toxicity to *Daphnia magna*, suggested that thallium toxicity in most natural waters does not need to account for the speciation of the dissolved thallium form owing to the lack of complexation of thallium(I) with both organic and inorganic ligands in natural waters.

Incorporating toxicity modifying factor(s) (TMF) into 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 owing 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.

The freshwater toxicity data set used to derive the HC_5 of the SSD assumed that observed adverse effects were caused by Tl(I). As discussed in section 7.1.3, it has been demonstrated that Tl(I) remained stable, whereas Tl(III) was converted to Tl(I) under experimental conditions during toxicity tests (Rickwood et al. 2015). The potential conversion of Tl(I) to Tl(III) in natural water by planktonic bacteria or the photooxidation of Tl(I) in the presence of aqueous cations (for example, Fe(III), Mn(IV), or As(V)) are not likely to be present under laboratory test conditions. The assumption that toxicity observed in studies can be attributed to Tl(I) when speciation has not been specified is therefore practicable and not overly conservative, even though Tl(III) has a noticeably higher toxicity than Tl(I). Although it has been suggested that the low thallium (ng/L) and high potassium contents of seawater should reduce thallium uptake and toxicity to marine organisms, phytotoxicity was still observed in certain marine algae species. The PNEC calculated for marine species applied a further assessment factor of 5 to account for the specific mode of action (that is, phytotoxicity in marine macroalga) in order to be protective of a wider variety of algae and aquatic plant species in the marine environment.

Since the available estimated field or laboratory model BAFs for higher trophic level organisms (for example, fish, invertebrates) were between 1000 and 1500, it has been determined that thallium does not meet the bioaccumulation criteria (that is, 5000) under the *Persistence and Bioaccumulation Regulations* of CEPA. As discussed in section 6.3, thallium is easily assimilated by various aquatic and soil-dwelling organisms and, most importantly, by plants. It therefore has the potential to accumulate, as evidenced by elevated thallium concentrations in organisms near sources of releases. Owing to contradictory data, there is uncertainty associated with the potential of thallium to biomagnify in both aquatic and terrestrial food chains. It is recognized that the current understanding of thallium bioaccumulation and consequential effects in environmental receptors is limited. Further collection of data is required 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

The human health assessment took into consideration those groups of individuals within the Canadian population who, due to greater susceptibility or greater exposure, may be more vulnerable to experiencing adverse health effects. For thallium and its compounds, Canadian human biomonitoring data in children, pregnant women and pregnant people, and specific Indigenous communities were used to inform consideration of these populations and take them into account in the risk assessment outcomes. The potential for cumulative effects was considered in this assessment by examining cumulative exposures to the moiety of thallium.

Thallium is a naturally occurring element that is present in environmental media in Canada (section 4.1). Total thallium concentration has been measured in indoor and outdoor air, drinking water distribution systems, and household dust (NAPS 2011; Health Canada 2016; Tugulea 2016; Rasmussen et al. 2022). However, 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 on the basis of concentrations measured in breast milk from Canadian mothers (n=1017) between 2008 and 2011 as part of the MIREC study (personal communication, email from the Bureau of Chemical Safety, Food Directorate, to the Existing Substances Risk Assessment Bureau, Health Canada, 2016; unreferenced).

The human health risks of thallium and its compounds were characterized using a scientific approach that is based on biomonitoring data, entitled the Biomonitoring-based Approach 2 (Health Canada 2016). The approach utilizes population-level biomonitoring data from large-scale surveys, such as the 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 (for example, 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 (for example, 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 regression correlations between external exposure and the biomarker concentrations (that is, 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 (that is, 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 (that is, 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 (that is, 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 urinary thallium concentrations in the general population of Canada and the United States were measured in the CHMS and the NHANES studies (Health Canada 2016), as well as in studies targeting specific subpopulations such as a First Nations Gwich'in community in Old Crow, Yukon (Drysdale et al. 2021), First Nations communities in Northwest Territories Mackenzie Valley (Ratelle et al. 2020), and the Inuit population in Nunavik, Quebec (Cirtiu et al. 2022) (Table 8-1). Thallium was detected in 99% of Canadians surveyed in the CHMS between 2009 to 2011, and concentrations were relatively similar across the Canadian population. Females had slightly higher concentrations of thallium than males, but this was not statistically significant (Health Canada 2013). Median urine levels of thallium in pregnant women surveyed in the CHMS were significantly lower than levels in non-pregnant females of reproductive age (Health Canada 2013; Walker 2016). Concentrations in First Nation and Inuit communities were similar to those in the CHMS

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). This value is supported by 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 HBM-I value is based on data from two key epidemiological studies in thallium-exposed workers and people living in the vicinity of a German cement factory (Schaller et al. 1980; Brockhaus et al. 1981). In an investigation of thallium-exposed workers, 128 males working in cement production in Germany submitted urine samples for examination. No adverse health effects attributable to thallium were observed in any of the subjects (Schaller et al.1980). An epidemiological study by Brockhaus et al. (1981)

investigated a group of the general population (n=1200, ages 1 to 85) living in the vicinity of a thallium-emitting cement factory in Lengerich, Germany. The study population included both children and pregnant women. Individuals were studied for signs of elevated exposure and symptoms associated with thallium overload. No correlations were found between urinary thallium levels and symptoms such as hair loss and dermal or gastrointestinal distress, which are all typical of thallium overload. However, a positive association was observed between thallium levels and self-reported symptoms such as insomnia, fatigue, weakness, nervousness, headache, psychological disorders, and neurological and muscular symptoms (Brockhaus et al.1981). The German Human Biomonitoring Commission also considered the results of a follow-up study conducted in the same region of Germany that evaluated developmental effects. The results of this study indicated that a causal relationship between thallium exposure and congenital birth defects is unlikely in this population (Dolgner et al. 1983).

The median and the 95th percentile of urinary thallium concentrations in Canada and the United States are compared to the HMB-I values in Table 8-1.

Table 8-1. Adjusted concentrations of total thallium in urine (µg/g creatinine) in the Canadian and U.S. population

Survey population	Age (years)	Median (95% CI)	Geometric mean (95% CI)	95th percentile (95% CI)	HBM-I	Exceedance
CHMS Cycle 2[a, b] Canadian population (2009–2011)	3 to 79	0.20 (0.20–0.23)	0.22 (0.20–0.23)	0.55 (0.49–0.61)	6.4[h]	N
NHANES[c] United States population (2015–2016)	6 and older	0.161 (0.149–0.177)	0.1530153 (0.143–0.163)	0.435 (0.403–0.466)	6.4[h]	N
Northwest Territories Mackenzie Valley[d] (2016–2018)	6 and older	NR	0.13 (0.12–0.15)	0.37 (0.30–0.44))	6.4[h]	N
Old Crow, Yukon[e] (2019)	18 and older	NR	0.1213 (0.11–0.14)	0.2128 (0.19–0.24)	6.4[h]	N

Nunavik, Northern Quebec (2017) [f]	16 and older	NR	0.23 µg/L (0.20–0.25)[g]	NR	5 µg/L	N

Abbreviations: CI, confidence interval; HBM-1, human biomonitoring value level 1 (Germany); NR, not reported; N, no

[a] Health Canada 2013

[b] Cycle 2 of the Canadian Health Measures Survey (CHMS) covers the population 3 to 79 years of age living in the ten provinces and the three territories. Excluded from the survey's coverage are: persons living on reserves and other Indigenous settlements in the provinces; full-time members of the Canadian Forces; the institutionalized population; and residents of certain remote regions. All together, these exclusions represent less than 4% of the target population.

[c] CDC 2019

[d] Ratelle et al. 2020

[e] Drysdale et al. 2021

[f] Cirtiu et al. 2022. Reported concentrations in urine are not creatinine adjusted.

[g] Converted from nmol/L urine, where µg/L urine = nmol/L urine * 1×10^{-9} mol/nmol * molecular weight (204.38 g/mol) * 1×10^{6} µg/g

[h] Converted from 5 µg/L urine, where µg/g creatinine = µg/L urine *average urinary excretion volume per day (1.4025 L urine/day) / average grams of creatinine excretion per day (1.1 g cr/day), using data presented in Hays et al. 2010.

Data in Table 8-1 demonstrate that adjusted concentrations of total thallium in urinary creatinine 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 United States 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). The CHMS is not a targeted survey and thus does not target individuals with high metal exposure or those living near point sources of exposure. Although there are no biomonitoring data for children under 3 years of age and children aged 1 to 4 years have the highest dietary intakes (per body weight basis), the 95th percentile concentration in the Canadian population is more than 10-fold lower than the HBM-I value. In addition, the HBM-I value incorporated data from children aged 1 year and older. The hazard data set for thallium is relatively robust and 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 provides 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 assessment, there is risk of harm to the environment from thallium and its compounds. It is concluded 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 concluded 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.

Considering all the information presented in this assessment, it is concluded 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 concluded that thallium and its compounds meet one or more of the criteria set out in section 64 of CEPA.

It is also determined that thallium and its compounds meet the persistence criteria but not the bioaccumulation criteria as set out in the *Persistence and Bioaccumulation Regulations* of CEPA.

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Appendix A. Acute toxicity studies for thallium in fresh water

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

Group	Test organism	Endpoint	Value[b] (µg/L)	Reference
Fish	Bluegill (*Lepomis macrochirus*)	96 h LC_{50}	126 000[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}	3 200[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	Kiliç 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}	510	Tatsi et al. 2015
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; unreferenced)

Abbreviations: EC_{50}, the concentration of a substance that is estimated to cause some effect on 50% of the test organisms; LC_{50}, median lethal concentration.

[a] Geometric means were 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 were reported in mg/L.