WATER QUALITY GUIDELINE SERIES

Antimony Water Quality Guidelines for the Protection of Freshwater Aquatic Life

Technical Report

Ministry of Water, Land and Resource Stewardship

Water Protection & Sustainability Branch

No. WQG-21

The Water Quality Guideline Series is a collection of British Columbia (B.C.) Ministry of Water, Land and Resource Stewardship water quality guidelines. Water quality guidelines are developed to protect a variety of water values and uses including freshwater aquatic life, drinking water sources, recreation, livestock watering, irrigation, and wildlife. The Water Quality Guideline Series focuses on publishing water quality guideline technical reports and guideline summaries using the best available science to aid in the management of B.C.'s water resources. For additional information on B.C.'s approved water quality parameter specific guidelines, visit:

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EXECUTIVE SUMMARY

The B.C. Ministry of Water, Land and Resource Stewardship (WLRS) develops province-wide, ambient Water Quality Guidelines (WQGs) for substances or physical attributes that are important for managing both fresh and marine surface waters of B.C. WQGs do not have direct legal standing but are used to provide a basis for evaluating the quality of water, sediment, and aquatic biota and to inform resource management decisions.

The development of WQGs for aquatic life is based on the principle that guideline values are protective of all forms of aquatic life and all aquatic life stages over indefinite exposure (ENV, 2019). For some substances, both a long-term chronic and a short-term acute guideline are recommended as provincial WQGs, provided sufficient toxicological data are available. To meet a WQG, both of its components (i.e., chronic long-term and acute short-term) must be met. However, an exceedance of a WQG does not imply that unacceptable risks are present, but that the potential for adverse effects may be increased and additional investigation and monitoring may be warranted.

Antimony (Sb) is a non-essential trace metal that is relevant to B.C. While background Sb concentrations in B.C. are generally lower than the threshold for adverse effects to biota, anthropogonic activities such as mining and the use of flame retardants can increase Sb concentrations to levels that can be harmful.

B.C. previously adopted Australia and New Zealand's Sb guideline as a working water quality guideline (WWQG) for the protection of freshwater aquatic life and natural ecosystem functions (ANZECC, 2000). Since that time, additional studies have improved the understanding of Sb toxicity. This report documents the derivation of Sb WQGs for the protection of aquatic life in B.C. A literature search was conducted to develop an antimony aquatic toxicity database. The data collected met the requirement to develop Type A2 chronic and acute guidelines. Long-term and short-term species sensitivity distributions were used to estimate the concentration posing potential effects to 5% of species (HC_5) associated with chronic and acute exposures, respectively. Following the B.C. protocol for WQG derivation (ENV, 2019), assessment factors were applied to the HC_5 values to derive the final chronic and acute WQGs. Since there are insufficient Sb toxicity data for marine biota, this report provides the freshwater chronic and acute WQGs. More research is required to derive the WQGs for the protection of marine life.

The updated chronic long-term and acute short-term WQGs for total Sb for the protection of freshwater aquatic life are 74 and 250 µg/L, respectively. These values are for the sum of Sb (III) and Sb (V), two of the most common oxidative states found in the environment, (Table ES.1) and are applicable in all regions of B.C.

Table ES.1. Proposed Water Quality Guidelines

	WQGs – Total Sb (µg/L)	
Designated Use	**Long-Term Chronic WQG**	**Short-Term Acute WQG**
Freshwater Aquatic Life	74	250

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LIST OF ABBREVIATIONS

AES: Atomic Emission Spectroscopy

AF: Assessment Factor

AFS: Atomic Fluorescence Spectroscopy

B.C.: British Columbia

CABIN: Canadian Aquatic Biomonitoring Network

DOC: Dissolved Organic Carbon

EC_{10}: 10% Effective Concentration

EC_{50}: Median Lethal Concentration

EMS: Environmental Management System

ENV: British Columbia Ministry of Environment and Climate Change Strategy

HC_5: Median Hazardous Concentration Affecting 5% of the species

ICP-OES: Inductively Coupled Plasma-Optical Emission Spectroscopy

ICP-MS: Inductively Coupled Plasma-Mass Spectrometry

LC_{50}: Median Lethal Concentration

LOAEL: Lowest Observed Adverse Effect Level

LOEC: Lowest Observed Effect Concentration

MATC: Maximum Acceptable Toxicant Concentration

MDL: Method Detection Limit

PNEC: Predicted No-Effect Concentration

Sb: Antimony

UF: Uncertainty Factor

USEPA: United States Environmental Protection Agency

WLRS: Water, Land, and Resource Stewardship

WQG: Water Quality Guideline

1. INTRODUCTION

The British Columbia Ministry of Water, Land and Resource Stewardship (WLRS) develops province-wide ambient Water Quality Guidelines (WQGs) for substances or physical attributes that are important for managing both fresh and marine surface waters of British Columbia (B.C.). A WQG is defined as a scientifically derived numerical concentration or narrative statement considered to be protective of designated values in ambient conditions. WQGs provide a basis for water quality assessments and inform decision-making in the natural resource sector and may be derived for the protection of designated values, including aquatic life, wildlife, agriculture (livestock watering and irrigation), drinking water sources, and recreation.

In B.C., WQGs are developed to protect the most sensitive endpoint associated with a given value (e.g., aquatic life, wildlife, livestock). For substances with sufficient toxicological data, both short-term acute and long-term chronic guidelines are developed. Interim guidelines are developed when the available toxicological data are insufficient (CCME, 1999; ENV, 2019).

WQGs are typically based on toxicological studies conducted under laboratory conditions. There are several uncertainties associated with applying WQGs to field conditions, including:

- Laboratory to field differences in exposure conditions;
- Single contaminant tests in laboratories vs exposure to multiple contaminants in the field that may demonstrate additive, synergistic, or antagonistic effects;
- Toxicity of metabolites;
- Intra- and inter-specific differences between test species used to derive the WQG and those found in the field;
- Indirect effects (e.g., behavioral responses, food web dynamics);
- Laboratory studies conducted on partial life cycle studies, which may not include the most sensitive life stage;
- Delayed effects which may not occur within the life stage tested, or may occur across generations; and,
- Cumulative effects of the various stressors, such as habitat loss and climate change, that organisms in the field are faced with.

Given these uncertainties, WQGs are considered an estimate of a no-effect concentration (i.e., no effects are expected if exposure concentrations are below the WQG). An exceedance of the WQGs presented in this document, however, does not imply that unacceptable risks are present, but that the potential for adverse effects is increased and additional investigation and monitoring may be warranted. Therefore, ongoing ecological monitoring is encouraged to ensure the WQG is indeed protective under field conditions.

Antimony (Sb) is a non-essential trace metal that can adversely affect aquatic organisms. Exposure to Sb can decrease growth in algae and macrophytes (e.g., Hammel et al., 1998; Díaz et al., 2013). Acute exposure to Sb can cause mortality and chronic exposure can affect growth, reproduction and survival of fish, amphibians, and invertebrates (e.g., Birge, 1977; Borgmann et al., 2005; US EPA, 2014).

B.C. previously adopted Australia and New Zealand's Sb guidelines (ANZECC, 2000) as a working water quality guideline (WWQG) for the protection of freshwater aquatic life. Since that time, additional studies have improved the understanding of Sb toxicity. This report provides the scientific evidence and rationale for the updated B.C. Sb WQGs for aquatic life. The WQGs for freshwater aquatic life were derived following the guidance provided in B.C.'s aquatic life derivation protocol (ENV, 2019).

2. PHYSICAL AND CHEMICAL PROPERTIES OF ANTIMONY

Elemental Sb is a silvery white, brittle solid that is classified as both a metal and a metalloid. It is not considered an essential element nor a beneficial element but has many industrial applications, including the production of semiconductors, manufacturing of batteries, and production of flame-retardant materials (industrial applications are further discussed in Section 3). Antimony does not occur as a free metal in the environment and forms complex ions with organic and inorganic acids such as antimony pentasulfide (Sb_2S_5 or S_5Sb_2), antimony pentoxide (Sb_2O_5), antimony potassium tartrate ($C_8H_{10}K_2O_{15}Sb_2$), antimony trichloride ($SbCl_3$), antimony trioxide (Sb_2O_3), antimony trisulfide (Sb_2S_3), and stibine (SbH_3), which have all gained research interest due to their industrial uses (ATSDR, 2019). Elemental Sb is stable under ordinary conditions, while antimony-containing substances have low volatility (HSDB, 2016).

Antimony can exist in four oxidation states (-3, 0, +3, and +5) where Sb(III) and Sb(V) are the most common and stable oxidation states in biological and environmental media, gaining the most research interest (ECCC & HC, 2020). In the natural environment at typical pH values, Sb is present as soluble $Sb(OH)^{6-}$ (in oxic conditions) and as soluble $Sb(OH)_3$ (in anoxic conditions). Under reducing conditions, and in the presence of sulfur, insoluble stibnite, Sb_2S_3(s) (solid form) is formed at low to near neutral pH values. An in-depth review of the geochemical controls on Sb speciation in aquatic environments can be found in Filella et al. (2002a). The physical and chemical properties of Sb and relevant antimony-containing compounds are summarized in Table 2.1.

The water solubility of antimony-containing substances ranges from low (e.g., antimony oxide) to high (e.g., antimony potassium tartrate [APT] and antimony trichloride) (ECCC & HC, 2020; Filella et al., 2002a). Most of the dissolved pentavalent Sb introduced into natural waters rapidly precipitates out of solution as either antimony trioxide or antimony pentoxide (Health Canada, 1999). This has implications for the presence of Sb in the truly dissolved phase versus total concentrations in samples that include the particulate and colloidal Sb fractions.

Table 2.1. Physical and chemical properties of antimony and compounds (ATSDR, 2019)

Property	Information							
Chemical Name	Antimony	Antimony pentasulfide	Antimony pentoxide	Ammonium potassium tartrate	Antimony trichloride	Antimony trioxide	Antimony trisulfide	Stibine
CAS Registry Number	7440-36-0	1315-04-4	1314-60-9	28300-74-5	10025-91-9	1309-64-4	1345-04-6	7803-52-3
Chemical Formula	Sb	S_5Sb_2	O_5Sb_2	$C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$	Cl_3Sb	O_3Sb_2	O_3Sb_2	H_3Sb
Molecular Weight (g/mol)	121.75	403.80	323.5 (anhydrous)	333.93	228.11	291.50	339.69	124.77
Colour	Silvery white	Yellow	Yellow	Colorless	Colorless	White (senarmontite); colorless (valentinite)	Black (stibinite); yellow-red (amorphous)	Colorless
Physical State at 25 °C	Solid	Solid	Solid	Solid	Solid	Solid	Solid	Gas
Antimony Valence State	0	+5	+5	+3	+3	+3	+3	-3
Melting Point (°C)	630.5	75 (decomposes)	380 (decomposes)	100 (-½ mole H_2O)	73.4	656	550	-88
Boiling Point (°C)	1,325 – 1,750	No data	No data	No data	283	1,550 (sublimes); 1,425	1,150	-17
Density (g/cm^3) at 20°C	6.688	4.12	3.78	2.6	3.140 (at 25°C)	5.2 (senarmontite); 5.67 (valentinite)	4.64 (stibinite); 4.12 (amorphous solid)	2.204 (at -17°C)
Water Solubility at 20°C	Insoluble	Insoluble	Very slightly soluble	83 g/L (cold)	6,016 g/L (at 0°C)	Very slightly soluble	1.75 mg/L (at 18°C)	4.1 g/L (at 0°C)
Organic Solvent Solubility	No data	Insoluble	No data	Insoluble in alcohol; soluble in glycerine	Soluble in ABS alcohol, tartaric acid, methylene chloride, benzene, acetone	Soluble in tartaric acid, acetic acid, hydrochloric acid	Soluble in alcohol; insoluble in acetic acid	Soluble in carbon disulfide, ethanol
Industrial Use	—	Used as a red pigment and used in the vulcanization of rubber to produce red rubber.	Used as a flame retardant in ABS and other plastics, as a flocculant in the production of titanium dioxide, and is used in the production of glass, paint, and adhesives	Used in the treatment of schistosomiasis and leishmaniasis	Used as reagent in a test to detect vitamin A and related catenoids. Also used as an adulterant to enhance the louche effect in absinthe.	Used as a flame retardant in electrical apparatuses, textiles, leather, and coatings.	Used in safety matches, military ammunition, explosives, and fireworks. Also used in the production of ruby-colored glass and as a flame retardant in plastics.	Used in the semiconductor industry to dope silicon with small quantities of antimony via the process of chemical vapour deposition (CVD).

3. INDUSTRIAL AND ECONOMICAL IMPORTANCE OF ANTIMONY

Antimony compounds have been used in cosmetics, casting pottery, and in various medications since ~3,000 B.C. (Luz et al., 2018). Records from bogs (Shotyk et al., 2005) and Arctic polar ice cores (Barbante et al., 2004; Krachler et al., 2005) show a striking increase in Sb present in the environment since the Industrial Revolution due to its extensive use in industry (Telford et al., 2009). Today, Sb has a wide range of industrial applications and is a key ingredient for semiconductor devices such as infrared detectors and diodes, circuit boards, and electric switches. It is also alloyed with lead and other metals to improve their hardness and strength which is crucial for the production of batteries, bullets, and cable sheathing. Antimony compounds are also used to make flame-retardant materials, paints, enamels, high quality clear glass, and pottery (Filella et al., 2002a; Obiakor et al., 2017; Wilson et al., 2010).

Presently, trivalent antimony trioxide (Sb_2O_3) is the most commercially relevant processed form of the metalloid and is used in flame retardant and polyethylene terephthalate (polyester – a general-purpose thermoplastic polymer) production (Anderson, 2000). Trivalent Sb is also used as an additive in pigments, paints (oxides are used in white paint, while trisulfide and pentasulfide yield black, vermillion, yellow, and orange pigments), and ceramics (Anderson, 2000; Luz et al., 2018).

The majority of Sb released to the atmosphere from anthropogenic sources is from metal smelting and refinement, refuse and sludge incineration, combustion of coal, and road traffic (RIVM, 2012). Major anthropogenic emissions (in order of importance globally) result from fuel combustion, nonferrous metal production and refuse incineration (Pacyna and Pacyna, 2001). Globally, incineration activities are estimated to release approximately half as much antimony as smelters (ATSDR, 1992). Conversely, in Canada a major source of Sb is as a by-product from lead mining and smelting operations in British Columbia and New Brunswick (ECCC & HC, 2010; Health Canada, 1999). The combustion/incineration processes associated with smelting, fuel combustion and other processes transform Sb compounds to diantimony trioxide regardless of the initial form of Sb (RIVM, 2012). These activities may result in long-range transport of Sb far from its source.

4. ENVIRONMENTAL FATE AND TRANSPORT OF ANTIMONY

Antimony is ubiquitously present in the environment from natural processes (i.e., sea spray, windblown dust, volcanic eruption, and forest fires; [ECCC & HC, 2020]) and anthropogenic sources (i.e., fuel combustion, metal smelting and refinement, and refuse and sludge incineration [Pacyna and Pacyna, 2001; RIVM, 2012]). It ranks 63rd in elemental abundance in the earth's crust (concentrations ranging from ~0.2 to 0.5 µg/g [Anderson, 2000; Filella et al., 2002a; Filella and May, 2003; Health Canada, 1999]), and it tends to concentrate in sulfide ores. It is seldom found in the environment as a pure element, but rather, often found as trivalent and pentavalent sulfides and chlorides (Health Canada, 1999), co-occurring with copper, lead, and silver (Anderson, 2000). The oxidized form of Sb, Sb(V), is expected to be the more stable form in the environment (Mitsunobu et al., 2006). Similarly, inorganic species are expected to be more present than organic species of Sb in most environmental systems (Wilson et al., 2010). Many researchers have reported significant enrichment of Sb in various cores (e.g., peat, sediment, soil, etc.), indicating significant anthropogenic fluxes of this metal have exceeded natural ones for more than 2,000 years (Barbante et al., 2004; Krachler et al., 2005; Shotyk et al., 2005; Telford et al., 2009).

4.1 Air

Antimony is emitted to the atmosphere principally in the form of fine particulate matter. This fine particulate Sb may be water soluble (ECCC & HC, 2010), resulting in Sb enriched rain being transported long distances. Dry deposition may also occur, although to a lesser degree (Stossel and Michaelis, 1986).

4.2 Water

Geological weathering, oxidation, and microbial processes convert primary Sb mineral phases (predominantly sulfides) to forms that are more soluble in water and more mobile in the environment (ECCC & HC, 2020; Herath et al., 2017). The fate of Sb in the aquatic environment is determined by several factors, including redox conditions, pH, sorptive interactions, and biologically-mediated methylation/demethylation reactions (Health Canada, 1999). Dissolved-phase Sb exists almost exclusively in a combination of +3 and +5 valency states (i.e. Sb (III) and Sb(V)) (RIVM, 2012).

Based on thermodynamics, Sb should almost exclusively be present as Sb(V) in oxic environments (most likely present as dissolved $Sb(OH)_6^-$ [Filella et al., 2002b]), or as Sb(III) in anoxic systems (Herath et al., 2017; RIVM, 2012). However, the analyses of different Sb species in aqueous samples have routinely shown the presence of both stibnic (3+) and stibnous (5+) compounds, most likely the result of slower reaction kinetics, and/or lack of complete homogeneity in aqueous samples such that a range of redox conditions are present at a microscopic scale.

The form of antimony predicted from thermodynamics over a broad range of redox conditions (eH) and pH in aqueous systems is illustrated in Figure 4.1 (Filella et al., 2002a). Aqueous Sb chemical speciation is generally more sensitive to redox conditions than pH per the large number of different species favoured under an eH range of approximately -300 mv to +300 mV. Sb_2S_3, the mineral stibnite, is generally insoluble unless subsequently oxidized, and is thus shown to occur as a solid in Figure 4.1. The various Sb oxyanions tend to be negatively charged at high pH values and positively charged at pH < 2 (i.e. for $Sb(OH)_2^+$).

Most of the dissolved antimony (both Sb(III) and Sb(V)) that might be discharged to natural waters soon precipitates out of solution and is removed by sedimentation (Health Canada, 1999). Prior to sedimentation, antimony is moderately mobile in surface waters (oxidizing conditions, pH 5-8) (Filella et al., 2002b, 2002a; Garrett, 2013).

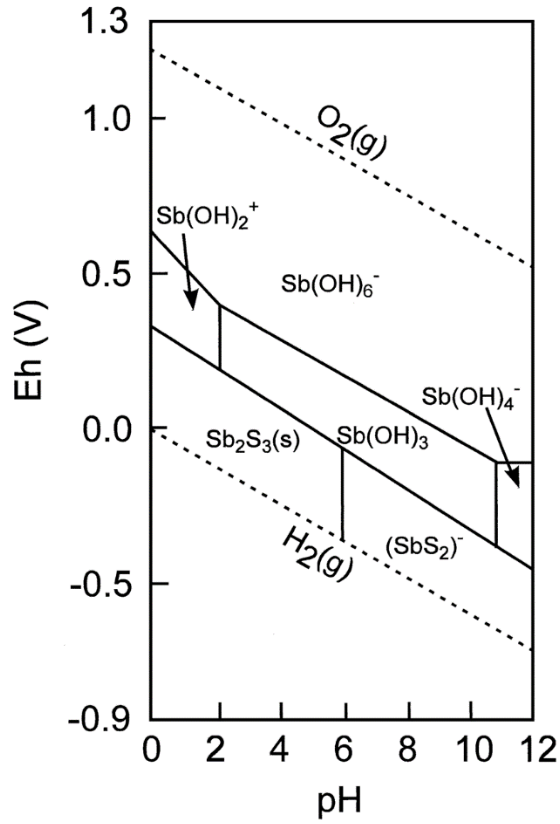

Figure 4.1. The relationship between Eh (redox potential) and pH (activity of hydrogen ions) as it relates to antimony speciation in a dissolved state. Figure adapted from Filella et al. (2002a).

Interactions with natural organic matter can also control dissolved Sb concentrations in aqueous phase (Filella and May, 2003; Filella and Williams, 2012) where Buschmann and Sigg (2004) reported that over 30% of total Sb(III) may be bound to aquatic humic acids through phenolic and carboxylic functional groups. Microorganisms and algae also appear to play a crucial role in several biotransformation mechanisms, such as Sb(V) reduction, Sb (III) methylation, and Sb (III) oxidation. These microorganisms facilitate the conversion of Sb compounds between Sb(III) and Sb(V), in both inorganic and organic chemical forms (Filella et al., 2007; Li et al., 2016; Obiakor et al., 2017).

Microorganisms and algae also appear to play a crucial role in several biotransformation mechanisms, such as Sb(V) reduction, Sb (III) methylation, and Sb (III) oxidation. These microorganisms facilitate the conversion of Sb compounds between Sb(III) and Sb(V), in both inorganic and organic chemical forms (Filella et al., 2007; Li et al., 2016; Obiakor et al., 2017). Bacteria and algae have been demonstrated to oxidize Sb(III), while anaerobic bacteria in anaerobic freshwater sediment reduced Sb(V) (Obiakor et al., 2017). Microbe-mediated Sb oxidation and reduction is not yet fully understood, and the extent of biologically related transformation, particularly how it relates to detoxification in aquatic biota, needs further investigation.

4.3 Soil

Given its negligible vapour pressure and limited water solubility, antimony will tend to remain in soil rather than migrate into other environmental media, such as air or water (ECCC & HC, 2010). Antimony incorporated in mineral lattices within the soil is inert and therefore unlikely to be bioavailable (RIVM, 2012). Antimony is retained in the soil primarily through adsorption and can sorb to clay minerals, or to oxides and hydroxides in the soil (Wilson et al., 2010). Sorption was found to be highly dependent on pH;

at pH levels < 7, Sb(V) was found to be almost completely sorbed, while Sb (III) was found to be sorbed at pH levels < 10 (ATSDR, 2019). The effect of pH on antimony mobility appears to be mediated by the hydrous oxides; these oxides assume an increasingly negative charge with increasing pH (resulting in weaker sorption of the negatively charged $Sb(OH)_6^-$) (ECCC & HC, 2010). pH changes can also influence the valence of antimony (with higher pH values favouring oxidation) and the solubility of solid Sb (ECCC & HC, 2010).

Antimony can be taken up by plants through the roots and via surface deposition from aerosols. Surface deposition is the major pathway for soil-to-plant transfer of antimony in field conditions (Tschan et al., 2009), as Sb in the soil matrix is more tightly sorbed.

5. ANALYSIS OF ANTIMONY IN ENVIRONMENTAL SAMPLES

Both total and dissolved Sb can be analysed in water samples. Dissolved Sb analysis refers to that concentration which passes through a 0.45 µm filter, while total Sb analysis includes the dissolved fraction and any Sb associated with particulates such suspended sediments or organic carbon particulates.

According to Fillela et al. (2002b), both inductively coupled plasma (ICP) atomic emission spectrometry (AES) and mass spectrometry (MS) methods are widely used, with ICP-MS having fewer spectral interferences and a lower detection limit (picogram per litre range). The B.C. Environmental Laboratory Manual (Austin, 2015) recommends four different common laboratory techniques for the measurement of Sb in environmental samples Table 5.1.

Table 5.1. Laboratory analysis methods for antimony

Laboratory Technique	Matrices	Detection Limits (µg/L) (Range)
Atomic Absorption – Direct Aspiration	Water, wastewater, and marine water	MDL = 200 (200 – 40,000)
Atomic Absorption – Gaseous Hydride	Water, wastewater, and marine water	MDL = 0.1 (0.1 – 10)
Atomic Absorption – Gaseous Furnace	Water, wastewater, and marine water	MDL = 3 (3 – 300)
Atomic Emission – Inductively Coupled Argon Plasma (ICAP)	Water, wastewater, and marine water	MDL = 50 (50 – 1,000,000)

Note: Information adapted from Austin (2015).

The determination of Sb species present in surface waters and other environmental compartments remains analytically complex and challenging, making it difficult to distinguish between Sb(III) and Sb(V) compounds or of the various organoantimony complexes such as simple methylated forms.

6. BACKGROUND CONCENTRATIONS OF ANTIMONY IN BRITISH COLUMBIA

Antimony is a naturally occurring element in aquatic and terrestrial ecosystems, therefore, background concentrations must be considered when deriving provincial Sb WQGs (ENV, 2019).

6.1 Background Concentrations of Antimony in British Columbia Surface Waters

Background (i.e., from non-impacted sites) Sb concentrations vary across B.C. as a function of local geology and hydrology, therefore, a regional approach was used to estimate background Sb concentrations in aquatic environments following methods used in recent WQG derivation documents (ENV, 2019; 2021).

6.1.1 Methods for Estimating Background Concentrations of Antimony in British Columbia Surface Waters

Background Sb concentration data in B.C. surface waters were taken from two sources: the B.C. Environmental Management System (EMS) database and the Canadian Aquatic Biomonitoring Network (CABIN) database. EMS does not identify reference stations, so the database was screened to create a sub-set of water quality stations known to be minimally impacted. To do this, “background” water quality sampling stations that were sampled at least three times over the last 24 years for any water quality parameter (1998/01/01 to 2022/10/31) were extracted. Next, the list of stations with location information was given to ENV environmental impact assessment biologists to identify sites that they considered minimally impacted by human activities. No strict definition of ‘minimally impacted’ was given to the biologists and station selection was left to their professional judgement. The list of minimally impacted stations was then used to extract Sb water quality data from the EMS database.

The dataset underwent several additional automated and manual data cleaning steps summarized below:

- For lakesamples, if samples were available at multiple depths, only samples from the surface were included;
- non-detect results with a MDL of 5 µg/L or higher were removed as these would influence the results of the analysis; and
- samples were excluded where results were missing or reported as 0.

Arithmetic means were calculated for laboratory replicates (analytical replicates taken from one field sample) with the MDL substituted for values below detection. All field replicates were included as independent samples.

The resultant data set was augmented with samples collected by ENV and Environment and Climate Change Canada (ECCC) at B.C. reference stations as part of the CABIN program. CABIN reference stations are located on stream reaches minimally impacted by anthropogenic activities and are generally sampled once during the late summer/early fall low flow period.

The results from each station were given equal weight within an ENV administrative region by calculating the mean Sb concentrations for each station. Station means were calculated using four different approaches depending on the number of samples above (detects) and below (non-detects) the MDL (Table 6.1). A value of ½ the minimum MDL was used to represent station means when all samples were below the MDL (Group 1). The minimum MDL was chosen to account for decreasing MDLs over time. For stations with less than three detects, ½ of the MDL was substituted for non-detect values and the arithmetic mean of all station results was calculated (Group 2). Regression on order statistics (ROS) was used to calculate an estimate of the mean for stations that had a mixture of non-detects and detects with at least three detected values (Huston and Juarez-Colunga, 2009; Group 3). Although Huston and Juarez-Colunga (2009) state that ROS can be used on sample sizes > 0, a minimum of three detects is required to calculate a valid regression using the NADA package (Lee, 2017) in R (R Core Team, 2018). The arithmetic mean was calculated for stations where all samples were above the MDL (Group 4). Statistics to summarize the distribution of station means (median, the 10^{th} and 90^{th} percentile) were calculated for each ENV region.

Table 6.1. Statistical approach used to calculate station means.

Group	Conditions	Approach	Total Stations	Total Samples
1	% non-detects = 100	½ of minimum station MDL	39	242
2	0 < % non-detects < 100 AND # detects < 3	Substitute ½ MDL for non-detects and calculate arithmetic mean for all samples	42	295
3	0 < % non-detects < 100 AND # detects ≥ 3	Regression on order statistics	91	4,409
4	% non-detects = 0	Arithmetic mean	55	566

6.1.2 Background Concentration Results

Data from 227 EMS and CABIN stations with a total of 5,512 results were used to characterize background Sb concentrations across B.C. (Appendix 1). The distribution of total Sb concentrations by ENV administrative region is summarized in Table 6.2 and Figure 6.2. The median of station means ranged from 0.0162 µg/L (Vancouver Island) to 0.0911 µg/L (Kootenay Region) (Table 6.1).

Of the 227 stations, 77 stations were on lakes and 150 were on rivers. The median of the distribution of station means in rivers (0.055 µg/L) was very close to that of lakes (0.045 µg/L) (see Figure 6.2).

Table 6.2. Summary statistics for station mean total antimony at selected minimally impacted stations in British Columbia by region.

Region	Number of Stations	Sample No.	Date Range	Concentration Range Across all Samples (µg/L)	MDL Range Across all Samples	% Samples < MDL	Distribution of Station Means (µg/L)		
							Median	10^{th} Percentile	90^{th} Percentile
Cariboo	59	1,815	1998 - 2022	0.001 - 30	0.001 - 0.5	37.5	0.0694	0.026	0.25
Kootenay	14	277	1998 - 2022	0.021 - 70	0.1 - 1	72.6	0.0911	0.041	2.285
Lower Mainland	7	57	2002 - 2022	0.005 - 3.37	0.005 - 0.5	19.3	0.0441	0.011	0.776
Okanagan	22	737	1998 - 2022	0.005 - 70	0.005 - 0.2	79.8	0.0184	0.007	0.072
Omineca	12	467	2003 - 2022	0.001 - 3.39	0.001 - 0.1	3.0	0.0388	0.025	0.075
Peace	8	99	2008 - 2022	0.02 - 0.158	0.02 - 0.1	5.1	0.0895	0.033	0.102
Skeena	35	986	1999 - 2022	0.001 - 60	0.001 - 0.5	20.2	0.02	0.01	0.228
Thompson	21	330	1999 - 2018	0.005 - 10	0.005 - 3	46.7	0.0209	0.01	10
Vancouver Island	49	744	1998 - 2022	0.005 - 70	0.005 - 0.2	41.0	0.0162	0.01	0.031

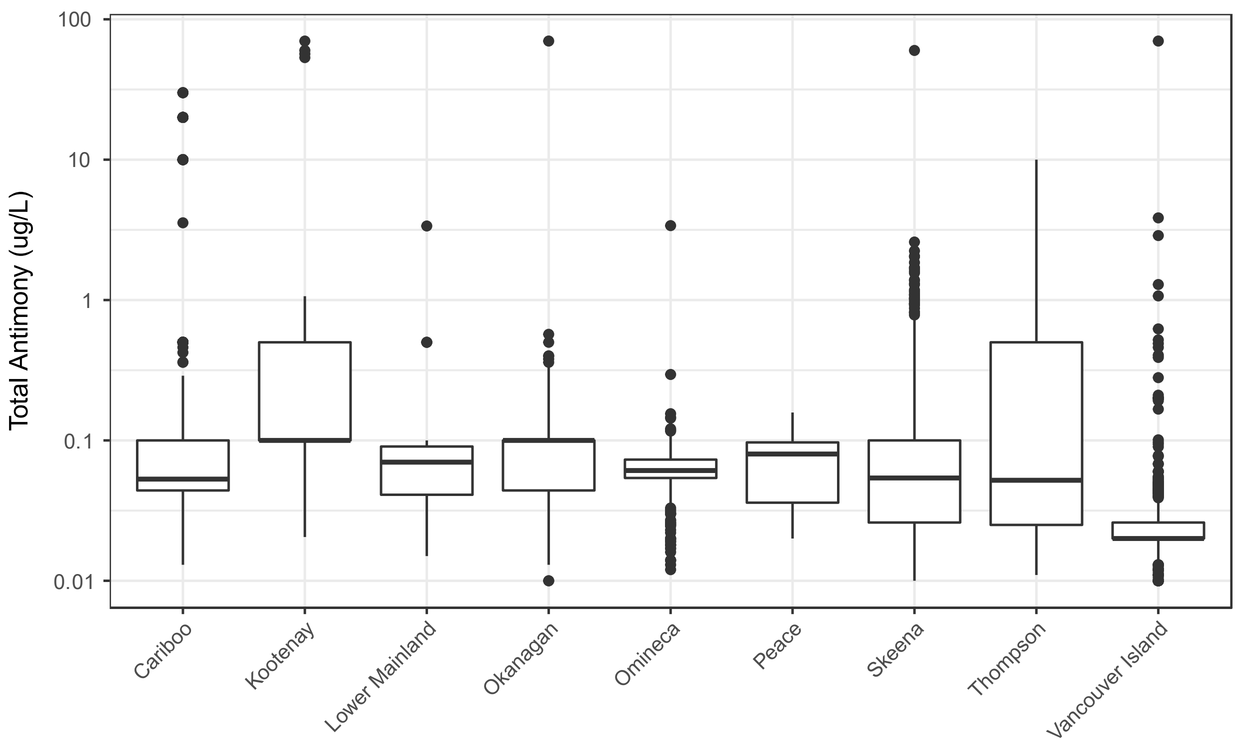

Figure 6.1. Distribution of station mean total antimony at selected minimally impacted stations in British Columbia by region.

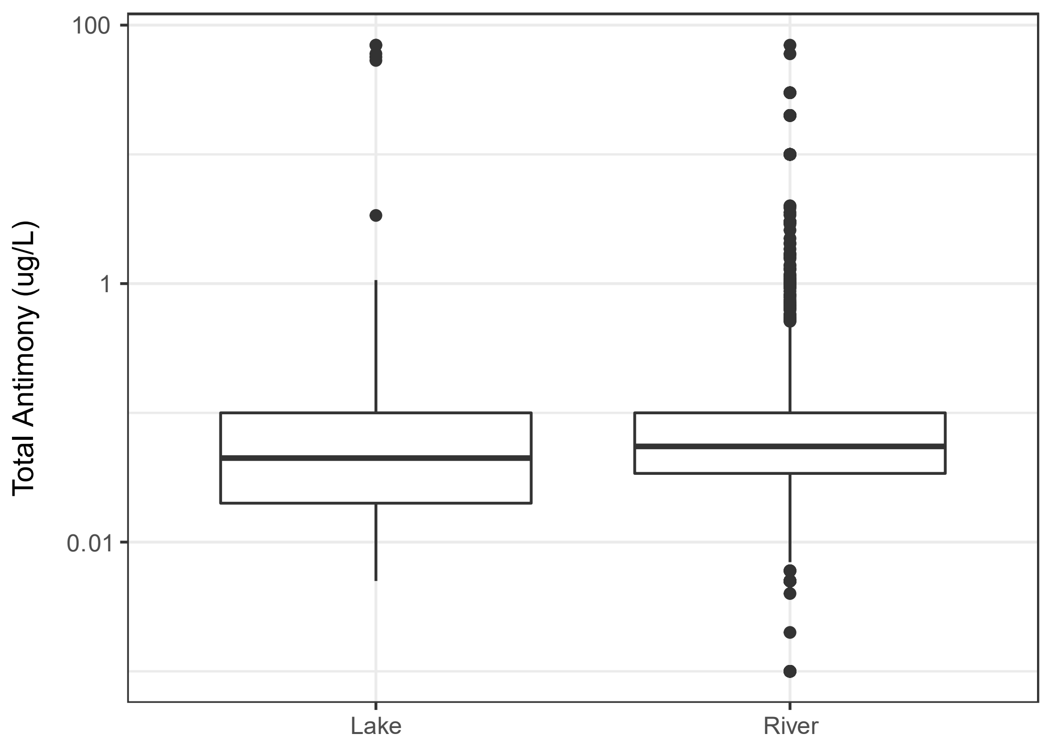

Figure 6.2. Distribution of station means for lakes and rivers for total antimony.

7. TOXICITY OF ANTIMONY

Antimony is not considered to be an essential element for life and can cause adverse effects to biota if present at elevated concentration in the environment. The potential effects can range from changes in growth and reproduction, as well as normal physiological function including swimming, development, respiratory behaviour, and eventually death (Bayley and Dell'Omo, 2002; Hook et al., 2014; Scott and Sloman, 2004). The mechanisms of antimony toxicity are still not completely understood (Obiakor et al., 2017). The original understanding was that Sb toxicity was indirect, through the interaction with protein and nonprotein homeostasis and inhibition of DNA replication (Gebel, 1997; Gebel et al., 1998; Schaumloffel and Gebel, 1998). The primary pathway for toxicity has been proposed to be passive diffusion through a cellular lipid bilayer, resulting in Sb uptake, distribution, and toxicity at the site of action, resulting in genotoxicity (Gebel, 1997; Stemmer, 1976). The general mechanism of Sb genotoxicity can be summarized as the uptake of Sb(V) by cells, and Sb(V) reducing to Sb(III) or remaining as Sb(V) depending on the pH (Hansen et al., 2011; López et al., 2015; Phillips et al., 2016). The reduced Sb(III) is thought to then react with thiols of proteins in the cell cycle, or react with DNA biochemical pathways, thereby impairing nucleotide repair (Grosskopf et al., 2010) and ultimately inhibiting enzyme function and cell repair.

Numerous studies have evaluated the potential toxicity of Sb and its different speciation (III and V) on numerous organisms including algae, macrophytes, invertebrates, aquatic invertebrates, fish, and amphibians (e.g. Birge, 1977; Hammel et al., 1998; Borgmann et al., 2005; Obiakor et al., 2017; Kennedy, 2020; Kennedy, 2023). Most of the research has been conducted on Sb (III) as it has been classified as a potential carcinogen (IARC, 2012, 1989) and Sb(III) species are often reported to be more toxic to aquatic life than Sb(V) species (Filella et al., 2012). Obiakor et al. (2017), however, caution against over-generalization since there are published exceptions to this. Based on thermodynamic considerations, antimony is expected to occur in its trivalent form under low redox conditions and in its pentavalent form under well oxygenated conditions; however, both oxidation states have been routinely quantified in aqueous samples under both oxic and anoxic conditions.

It is important to note that studies exploring the toxicity of Sb often use a wide variety of carrier compounds including; $C_8H_4K_2O_{12}Sb_2 \times 3H_2O$ (Nam et al., 2009), $SbCl_3$ (Chen and Yang, 2007), Sb_2O_32SbCl (Den doore de Jong and Roman, 1965), which could influence the effects observed and make it difficult to discern whether one oxidation state of Sb is more toxic than the other (Obiakor et al., 2017). For example, Takayanagi (2001) exposed marine fish (*Pargus major*) to Sb (III) and Sb (V) in the forms of $SbCl_3$ and $SbCl_5$, respectively, and demonstrated that Sb (V) was more toxic than Sb (III), whereas similar toxicities were observed between the two oxidations states was supplied in the forms of $SbCl_3$ and $K[Sb(OH)_6]$, respectively. This highlights the need to account for co-occurring substances when interpreting Sb toxicity results. In a recent study, Kennedy (2023) compared the toxicity of Sb (III) and Sb (V) on one algae species (*Chlorella vulgaris*) two invertebrate species (*Ceriodaphnia dubia and Hyalella Azteca*) and one fish species (Sockeye Salmon; *Oncorhynchus nerka*). The salts used for this study were antimony (III) chloride and antimony (V) chloride. No significant difference was observed in toxicity of two forms of Sb in any of the above-mentioned species (Kennedy, 2023).

7.1 Effects on Algae

The adverse effects of elevated antimony on algal species include chlorophyll *a* reduction (US EPA 1988) and growth inhibition (Den doore de Jong and Roman, 1965; Hammel et al., 1998; Nam et al., 2009; Obiakor et al., 2017; Oorts and Smolders, 2009; Sauvant et al., 1995a, 1995b; US EPA, 2014, 1977). A variety of algal species have been used in the evaluation of antimony toxicity, and hence a range of concentrations have been shown to have toxic effects.

Freshwater chronic EC_{50} values for growth were 7,787 and 10,685 µg/L for *Chlorococcum infusionum* and *Scenedesmus subspicatus*, respectively (Hammel et al., 1998), while *Pseudokirchneriella subcapitata* had an MATC value for growth ranging from 723 to 2,910 µg/L (US EPA, 2014). No studies that assess acute toxicity in algae were included in this report as they did not meet the acceptable criteria.

7.2 Effects on Macrophytes

Published results for antimony toxicity were available for only one aquatic vascular plant (*Fontinalis antipyretica*), recording adverse effects on growth following a 22 day exposure to $SbCl_3$ (Díaz et al., 2013). The range of toxicity thresholds is reflective of the limited dataset. The study yielded a no-effect level concentration (NOEC) of 1000 µg/L, a low-effect level concentration (LOEC) of 10,000 µg/L, a maximum acceptable toxicant concentration (MATC) of 3,162 µg/L, and an effective concentration (EC_{50}) of 4935 µg/L.

7.3 Effects on Invertebrates

Antimony ecotoxicity data were obtained for a total of eight different species of invertebrates (including crustaceans, *Hydra*, snails, and midges) from the scientific literature. Studies predominately recorded mortality only, although growth and reproduction were also recorded in some tests.

A wide range of acute toxicity threshold values (LC_{50}'s) are present in the invertebrate dataset. Acute mortality (LC_{50}) was measured at concentrations ranging between 500 µg/L (*Hydra oligactis*) to 21,600 µg/L (*Hyalella azteca*) (TAI, 1990). Variability in the measured LC_{50} values could stem from a variety of factors, including non-standard tests, and inter-species variability.

The chronic toxicity dataset includes a variety of different threshold values for aquatic invertebrates (i.e., IC_{50}, LC_{20}, LC_{50}, LC_{10}, LC_{15}, LOEC, NOEC, and MATC). LOEC values ranged from 800 µg/L (*C. dubia*) to 4,160 µg/L (*D. magna*), and MATC values ranged from 2,330 µg/L (*D. magna*) to 3,218 µg/L (*D. magna*). The majority of tests focused on mortality and/or reproduction as the final endpoint, while others measured impacts on growth.

7.4 Effects on Fish

The reported effects of antimony on fish include mortality, reduced growth (length and weight of larvae, yolk sac length), reproductive impacts (hatchability, abnormal larvae), oxygen consumption, blood cell deformation, metabolic enzyme activities, and concentrations of ions in the body (Na, K, Ca, Mg). A total of 13 studies were included from the literature that looked at acute and/or chronic antimony effects to 8 different fish species, including salmonids (sockeye and rainbow trout, all native or introduced to BC), and other temperate fish.

The LC_{50}'s ranged between 14,050 µg/L (*Cyprinus carpio*) and 25,800 µg/L (*Lepomis macrochirus).* As with invertebrates, variability in acute toxicity values could stem from a variety of factors including different forms of antimony (Sb (III) vs Sb (V)), the use of non-standard test methods, and inter-species variability.

There are six chronic studies that present chronic toxicity thresholds values for fish. Chronic no-effect threshold values ranged from 7.5 µg/L (*Pimephales promelas*; embyros) to 12,800 µg/L (*Oncorhynchus nerka*) and low-effect threshold values ranged from 2310 µg/L (*Pimephales promelas*; embyros) to 25,600 µg/L (*Oncorhynchus nerka*). A single study was found that looked at chronic effects of antimony on marine fish.

7.5 Effects on Amphibians

A single study investigated the long-term effects of antimony exposure on amphibians. Birge (1977) exposed narrow-mouthed toads (*Gastrophryne carolinensis*) to a variety of different metals, including antimony (as $SbCl_3$). Daily examinations looked for mortality and teratogenesis (malformations in the larval stage). Based on the results of these bioassays, an LC_{50} of 300 µg/L and an LC_1 of 3.8 µg/L were calculated.

8. ANTIMONY TOXICITY-MODIFYING FACTORS

Toxicity Modifying Factors (TMFs) are variables or conditions that may predictably alter the bioavailability and/or toxicity of a substance (e.g. metal/metalloid) by affecting the form of the substance in the aqueous environment (ENV2019). This includes the various determinants of the degree of solubility of a substance, its tendency to occur in a freely dissolved form or in association with colloidal and particulate matter, its chemical oxidation state, and its ionized form. TMFs may be incorporated into B.C. WQGs, and result in conditional and more site-specific applications of the WQGs, provided there is sufficient scientific supporting evidence for consistent relationships between TMFs and alterations in substance bioavailability and/or toxicity. Generally accepted TMFs that apply to some substances include pH, water hardness, temperature, and various measures of natural organic matter (NOM) such as the dissolved organic carbon (DOC) concentration.

Filella and Williams (2012) provided a review of the factors that influence the presence of Sb in aquatic systems as freely dissolved, complexed with 'simple' or lower molecular weight inorganic or organic ligands, complexed with large (generally organic) macromolecules such as humic and fulvic acids, or adsorbed onto suspended particulate matter. Similar to arsenic, Sb (IV) appears to have a very low affinity for complexation with NOM (Filella et al., 2012). Negatively charged Sb species are not expected to be readily attracted to the abundant negatively charged functional groups of NOM. However, as discussed by Filella and Williams (2012), some researchers have reported appreciable binding of Sb to NOM (Chen and Yang, 2007). They conclude that Sb complexation by humic-type substances is not significant at the pH and concentrations typical of surface waters.

Inorganic Sb species have generally been shown to have a strong tendency to sorb to iron and manganese oxyhydroxides in aqueous systems (under more oxic redox conditions that favor the presence of these oxyhydroxides themselves in their undissolved form). Published studies are available for laboratory investigations of quantitative rates of Sb sorption onto goethite, iron oxyhydroxide, hydrous Mn(IV) oxide, $Al(OH)_3$ gel, hydroxyapatite, diatomite, and bentonite (Filella and Williams, 2012). However, the quantitative relationships between pH or other TMFs and sorption potential cannot be generalized based on the current state of knowledge. A particularly important consideration for predictions of the mass of Sb complexed with suspended or bed sediments in comparison with freely dissolved Sb is the kinetics of sorption/desorption in addition to thermodynamic considerations. Kinetics are rarely considered in partitioning studies but nonetheless can have an important influence on the relative amounts of bioavailable and toxic forms of Sb under field conditions.

There are limited studies investigating the influence of pH, water hardness, various forms of NOM, temperature, or other potential TMFs on the toxicity of Sb on aquatic species. In a recent study Kennedy (2023) demonstrated that toxicity thresholds of Sb on survival and reproduction of *C. dubia* were not significantly different at various pH (i.e., 5.5, 7, and 8.5). Given the limited information, it is not feasible to include TMFs for derivation of a B.C. WQG for Sb.

9. ANTIMONY WATER QUALITY GUIDELINES FROM BRITISH COLUMBIA AND OTHER JURISDICTIONS

A brief review was completed of guidelines or similar types of generically applicable thresholds for protection of aquatic life that have been developed in other (Table 9.1). Fora detailed review of existing Sb environmental quality guidelines in various international jurisdictions, please see is provided by Bagherifam et al. (2019).

Table 9.1. Comparison of antimony water quality guidelines and other threshold of effects levels.

Australia and New Zealand	9 µg/L - Sb(III) freshwater aquatic life 270 µg/L - Sb(III) marine aquatic life	(ANZECC, 2000)
Canada	113 µg/L - Sb(III) as Sb_2O_3	(ECCC & HC, 2010)* Predicted No Effects Concentration (PNEC) for Aquatic Life, derived in support of a screening assessment for antimony trioxide under the Canadian Environmental Protection Act. PNECs derived from the lowest acceptable literature value as determined by EURAS: *see below.*
Europe	110 µg/L - Sb(III) as Sb_2O_3	EURAS (European Center for Risk Assessment) – Oorts and Smolders (2009): risk-based threshold developed under framework of European Existing Substances Regulation (793/93/EEC). Value is based on chronic NOEC for fathead minnow divided by an uncertainty factor (“assessment factor”) of 10.
United States	354 µg/L – Acute Concentration of Concern (COC) 162 µg/L – Chronic COC	USEPA, (2014). Antimony Trioxide Chemical Risk Assessment under the Toxic Substances Control Act (TSCA). The Acute COC was derived as the 96-h LC50 of 1,770 µg/L for the cnidarian *Chlorohydra viridissima* divided by an uncertainty factor of 5. The Chronic COC was derived from the 30-d MSTC for growth of fathead minnows divided by an uncertainty factor of 10.

Note: *Part of the *Canadian Environmental Protection Act* process, not a guideline.

9.1 Previous B.C. Water Quality Guideline

Previously, the water quality guideline for antimony was a working water quality guideline of 9 µg/L for freshwater aquatic life and 270 µg/L for marine aquatic life adopted from ANZECC (2000). A guideline specific to B.C. waters had not been previously developed.

9.2 Canadian Water Quality Guidelines

The Canadian Council of the Ministers of the Environment has not developed a water quality guideline for antimony. As part of the *Canadian Environmental Protection Act* process, Environment and Climate Change Canada developed a benchmark for Sb (III) of 113 µg/L. This is technically not a guideline; however, it is presented here for illustrative purposes.

9.3 International Water Quality Guidelines

Australia and New Zealand have joint WQGs described as values that trigger a response (i.e., trigger values) if exceeded (ANZECC, 2000). Two guidelines were developed, specific to Sb (III); a freshwater aquatic life guideline of 9 µg/L and a marine aquatic life guideline of 270 µg/L.

The European union has developed an antimony water quality guideline, and the Netherlands has developed one specific to their waterbodies. The European Centre for Risk Assessment (EURAS) has developed a probable no-effect concentration (PNEC) of 110 µg/L for Sb (III).

10. WATER QUALITY GUIDELINES FOR FRESHWATER AQUATIC LIFE

WQGs for the protection of freshwater aquatic life were derived using the guidance in *Derivation of Water Quality Guidelines for the Protection of Aquatic Life in British Columbia* (ENV, 2019). A search of the current scientific literature for studies on Sb toxicity to freshwater aquatic organisms in water-only exposures under laboratory conditions was conducted which retrieved 40 studies. Only studies on Canadian species (indigenous and non-invasive exotic species) were selected and evaluated to determine if they were scientifically sound and of high-quality (ENV, 2019). Information on the test species, test conditions, experimental design, chemical and physical properties of the test water, statistical analyses, and negative control performance were reviewed. Studies were then classified as primary, secondary, or unacceptable based on the criteria given in ENV (2019). A summary of all short-term and long-term primary and secondary data, and the studies classified as unacceptable, is provided in Appendix 2.

The data points were further classified as chronic long-term or acute short-term, in accordance with published protocols (CCME, 1999; ENV, 2019). In total, two studies were classified as primary, 27 as secondary, and 16 as unacceptable (Appendix 2). From the primary studies, four long-term data points were selected, and 17 short-term and 84 long-term data points were selected from the secondary studies (Table 10.1). Some studies investigated effects for both short- and long-term durations and therefore included both data types. In addition, some studies investigated the toxic effects of Sb on multiple species belonging to one or more taxonomic group (Appendix 2). Table 10.2 lists all aquatic species represented in the toxicity database.

Table 10.1. Distribution of primary and secondary data points between different taxonomic groups.

Taxonomic group	Total number of studies	Short-term data points	Long-term data points			
			Growth	Reproduction	Survival	Total
Primary studies						
Invertebrates	1	0	0	0	1	1
Fish	1	0	1	1	1	3
Total	2	0	1	1	2	4
Secondary studies						
Algae	5	0	8	0	0	8
Macrophytes	1	0	4	0	0	4
Invertebrates	10	8	3	29	23	55
Fish	10	9	6	1	10	17
Total	18	17	21	30	33	84

Table 10.2. Aquatic species included in the antimony toxicity dataset.

Taxonomic Group	Common Name	Species	Primary/Secondary
Algae	Green Algae	*Chlorella vulgaris*	S
	Green Algae	*Chlorococcum infusionum*	S
	Green Algae	*Pseudokirchneriella subcapitata*	S
	Green Algae	*Scenedesmus subspicatus*	S
Macrophytes	Aquatic moss	*Fontinalis antipyretica*	S
Invertebrates	Amphipod	*Hyalella Azteca*	P & S
	Cladoceran	*Ceriodaphnia dubia*	S
	Hydra	*Chlorohydra viridissima*	S
	Hydra	*Hydra oligactis*	S
	Midge	*Chironomus tentans*	S
	Snail	*Physella gyrina*	S
	Water flea	*Ceriodaphnia dubia*	S
	Water flea	*Daphnia magna*	S
	Water flea	*Simocephalus mixtus*	P
Fish	Bluegill	*Lepomis macrochirus*	S
	Channel catfish	*Ictalurus punctatus*	S
	Common carp	*Cyprinus carpio*	S
	Fathead minnow	*Pimephales promelas*	P & S
	Sockeye salmon	*Oncorhynchus nerka*	S

10.1 Water Quality Guideline Derivation

In total long-term data on 12 species and short-term data on 12 species were classified as acceptable for the purpose of deriving a water quality guideline. The combined data, however, do not meet the requirements for derivation of a type A1 WQG due to lack of primary studies, required invertebrate groups, and lack of amphibian data (ENV, 2019). The available toxicity data do meet the minimum requirements for developing the type A2 long-term chronic and type A2 short-term acute WQGs, following ENV (2019) methods.

10.1.1 *Long-Term Chronic Water Quality Guidelines*

There are secondary and primary long-term studies for one B.C. resident aquatic plant species, four resident algal species, five resident invertebrate species, and three resident fish species (including two salmonid species) (Table 10.3). The acceptable long-term studies provide a total of 84 data points and include multiple endpoints and effect levels for different life-stages and test durations. The most sensitive endpoint from each study was selected for further use in guideline derivation. When there were multiple data points for the same species, life stage, endpoint and exposure duration, the geometric mean of the effect concentrations was used. From this process, no-effect (NOEC) estimates on two species, maximum acceptable (MATC) estimates on five species, effective concentration (EC_{10}/EC_{50}) estimates on three species, and lethal concentration (LC_{10}) on three species were selected for deriving the WQG (Table 10.3). The final set of data points used to generate the long-term chronic WQG limited consisted of only the studies that used Sb (III) in their toxicity tests. Both the consensus in the literature and the recent results of Kennedy (2023) support the fact that Sb (III) is more toxic than Sb (V) or at least of equal toxicity (Section 7) and therefore, this WQG will protect against both species of Sb.

The R package, *ssdtools* version 0.3.4 (Thorley and Schwarz, 2018) was used to estimate an HC_5 value using maximum likelihood estimation (MLE) and model averaging of six distributions (i.e., gamma, lgumbel, llogis, lnorm, lnorm lnorm, and weibull). The calculated HC_5 value is 445 µg/L (95th percentile CL: 175 and 1400 µg/L) (Figure 10.1).

To account for the sources of uncertainty associated with WQG derivation, an AF must be applied to the calculated HC_5 (ENV, 2019). The AF begins with a default value of five that may be reduced or increased depending upon the residual uncertainty of the WQG (ENV, 2019). The minimum AF to be applied to Type A WQGs is 2 to account for the extrapolation of laboratory testing to field conditions. The chronic data set fulfills the minimum number of species required for a type A2 guideline, but multiple uncertainties remain (Table 10.4) including the lack of data for Ephemeroptera (mayflies), Plecoptera (stoneflies), Trichoptera (caddisflies), and amphibians, no clear understanding of the mechanism of toxicity, lethal and effect data points are included in the SSD and no field studies of the long-term effects of elevated Sb on aquatic ecosystems. Particularly, lack of amphibian data is a major concern. No data exists for Canadian amphibian species that qualifies for WQG derivation. However, the only available data on amphibians (Section 7.5) shows a high sensitivity of amphibians to Sb. The data gaps described above, therefore, warrant a precautionary approach. For this reason, the AF of 6 was selected and applied to the calculated HC_5 resulting in a WQG of 74 µg/L for both Sb (III) and Sb (V).

The recommended long-term chronic WQG for Sb (both Sb(III) and Sb(V)) of 74 µg/L is ten times higher than the highest observed 90th percentile across sampling station means in B.C. (Section 6.1). Current research suggests an increase in Sb concentrations below the WQG will not affect aquatic life but given the low background concentrations in B.C., careful ongoing monitoring of sites experiencing elevated Sb concentrations is recommended.

Table 10.3. Data points used to develop the antimony long-term WQG for the protection of freshwater aquatic life.

Receptor Group / Species	**Selected toxicity test endpoint**	**Exposure duration**	**Effect value (µg/L)**	**Reference**
Plants/Algae				
Fontinalis antipyretica	MATC; Growth	22-d	3,162	Díaz et al., 2013
Chlorella vulgaris	NOEC, Growth	72-h	6,400	Kennedy, 2023
Chlorococcum infusionum	EC_{50}; Growth	72-h	7,787	Hammel et al., 1998
Pseudokirchneriella subcapitata	MATC; Growth	72-h	1,450*	Heijerick and Vangheluwe 2004 & LISEC, 2011
Scenedesmus subspicatus	EC_{50}; Growth	72-h	10,685	Hammel et al., 1998
Invertebrates				
Ceriodaphnia dubia	EC_{10}; Reproduction	8-d	805*	Kennedy, 2023
Physella gyrina	LC_{10}; Survival	21-d	2,506	Kennedy, 2020
Daphnia magna	MATC; Reproduction	21-d	2,330	US EPA 2014 (originally Heijerick and Vangheluwe 2004)
Hyalella azteca	LC_{10}; Survival	14-d	404	Kennedy, 2023
Fish – non-salmonid species				
Pimephales promelas	MATC; Survival	30-d	1,616	US EPA 2014 (originally Kimball, 1978)
Fish – salmonid species				
Oncorhynchus mykiss	NOEC; Survival	30-d	3,200	Kennedy, 2020
Oncorhynchus nerka	MATC; Survival	30-d	18,100	Kennedy, 2023

EC = effective concentration; d=days; and h=hours.

LC = lethal concentration;

* The reported effect concentrations are geometric means of similar data points (i.e., same species, same life stage, same endpoint and same exposure duration).

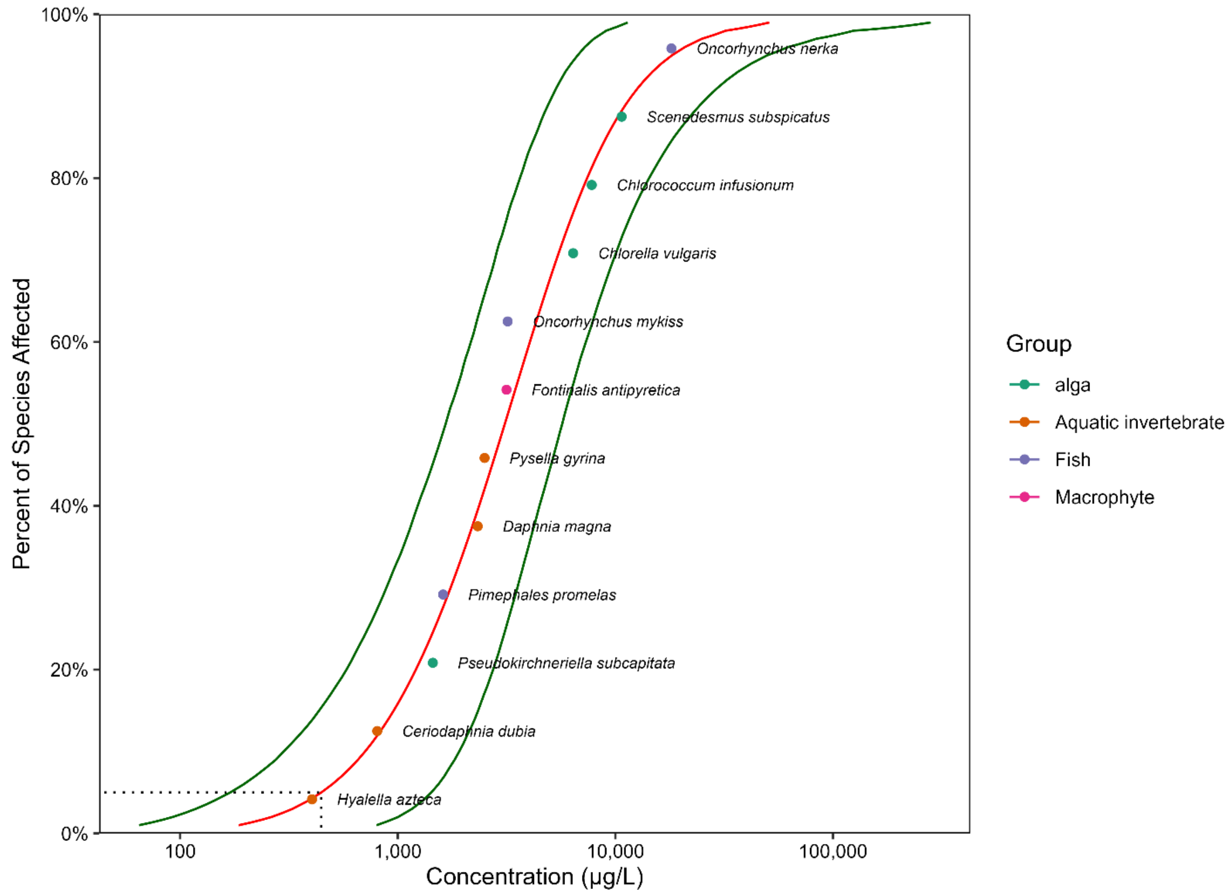

Figure 10.1. The distribution of no-effect/low-effect estimates from used to derive the antimony type A2 long-term water quality guideline for the protection of freshwater aquatic life.

The red line represents the fit of the averaged distribution, and the green lines represent the 95% confidence intervals of the fit. Dashed line denotes the HC_5 at the concentration of 445 µg/L.

Table 10.4. Considerations for determining the assessment factor for chronic long-term WQGs to protect freshwater aquatic life (ENV, 2019).

Consideration	**Evaluation**
The taxonomic and life stage representativity of the database.	No information on EPT or amphibians.
Knowledge of the toxicity modifying factors and mode of action of the substance.	There is limited information on the potential toxicity modifying factors of Sb and while there is a working hypothesis for mode of action, it remains supposition (see Sections 7 and 8).
Whether or not the SSD dataset includes no effect and low effect levels and/or lethal and non-lethal endpoints.	The SSD dataset does consist of no-effect data (i.e., NOEC), non-lethal data (i.e., MATC), and lethal data (LC_{50}).
Statistical uncertainties of the HC_5 estimate.	The HC_5 estimation is 445 with lower and upper 95th percentile CLs of the HC_5 are 175, and 1400 respectively. The average model has a good fit based on visual inspection with limited gaps between datapoints.
The level of agreement between the estimated HC_5 and mesocosm and/or field studies	No information is available on mesocosm and/or field studies.

10.1.1.1 Protectiveness of B.C. chronic antimony guidelines against long-term effects on survival

Further adjustment to the guideline to meet ENV's (2019a) protection clause was considered. While the 14-d lethality endpoint (LC_{10} = 404 µg/L) for *Hyalella azteca* is below the HC_5 value in Figure 10.1 (HC_5 = 445 µg/L), after the application of the assessment factor of 5, the proposed guideline of 74 µg/L is lower than the species' LC_{10}. Further, as per the protection clause, *Hyalella azteca* is not listed as a species at risk as defined by either the B.C Conservation Data centre for species that occur in B.C. or the Committee on the Status of Endangered Wildlife in Canada (COSEWIC). Finally, because no single taxon was clustered near the HC_5, additional AFs were not required to address the protection clause.

10.1.2 *Short-Term Acute Water Quality Guidelines*

There were 17 secondary, short-term acute studies (LC_{50} values) on seven Canadian resident invertebrate species and five Canadian resident and introduced fish species (Appendix 2). The available data met the minimum data requirements for the development of a type A2 short-term acute WQG. In cases where data were available for different life-stages, the LC_{50} that captured the lowest effect concentrations (i.e., most sensitive) was selected for further use in the guideline derivation. When there were multiple studies reporting results for the same species, life stage and duration, the geometric mean of effect concentrations was calculated and used instead of the individual values. The final set of data points used to generate the long-term chronic WQG consisted of 100% of studies that used Sb (III) in their toxicity tests. Since both the consensus in the literature and the recent results of Kennedy (2023) support the fact that Sb (III) is more toxic than Sb (V) or at least of equal toxicity (Section 7), this WQG will protect against both species of Sb.

Table 10.5. Data points used to develop the short-term acute antimony WQG for the protection of freshwater aquatic life.

Group/Species	Exposure duration	LC_{50} (µg/L)	Rank	Reference
Invertebrates				
Ceriodaphnia dubia	48-h	3,470	Secondary	US EPA, 1988 (originally Spehar, 1987)
Hydra oligactis	96-h	987*	Secondary	US EPA, 1988 (originally Brooke et al, 1986), Obiakor et al, 2017 (originally TAI, 1990)
Hyalella azteca	96-h	21,600	Primary	Obiakor et al, 2017 (originally TAI, 1990)
Chlorohydra viridissima	-	1,770	Secondary	Obiakor et al, 2017 (originally TAI, 1990)
Chironomus tentans	96-h	4,100	Secondary	Obiakor et al, 2017 (originally TAI, 1990)
Daphnia magna	96-h	12,100	Secondary	Obiakor et al, 2017 (originally Kimball, 1978)
Simocephalus mixtus	96-h	4,920	Primary	Obiakor et al, 2017 (originally, Nam et al., 2009)
Fish - non-salmonid species				
Lepomis macrochirus	96-h	25,800	Secondary	Obiakor et al, 2017 (originally Spehar, 1987)
Ictalurus punctatus	96-h	24,600	Secondary	Obiakor et al, 2017 (originally, TAI 1990)
Pimephales promelas	96-h	14,400	Secondary	Obiakor et al. 2017 (originally Brooke et al. 1986 and Tazwell and Henderson, 1960)
Cyprinus carpio	96-h	14,050	Secondary	Chen and Yang 2007
Fish - Salmonid Species				
Oncorhynchus mykiss	96-h	25,700	Secondary	Obiakor et al. 2017 (originally Brooke et al. 1986)

LC = lethal concentration; -h = hour.

*The reported effect concentrations are geometric means of results from comparable studies (i.e., same species, same life stage)

LC_{50} estimates of twelve species were used to derive the WQG. The R package, *ssdtools* version 0.2.0 (Thorley and Schwarz, 2018) was used to plot the toxicity data using MLE. Six distributions, (i.e., gamma, lgumbel, llogis, lnorm, lnorm lnorm, and weibull) were fitted to the toxicity data and a model averaging approach was taken to estimate an HC_5 value of 1250 µg/L (95th percentile CL: 369 and 4240 µg/L) (Figure 10.2) (ENV, 2019a).

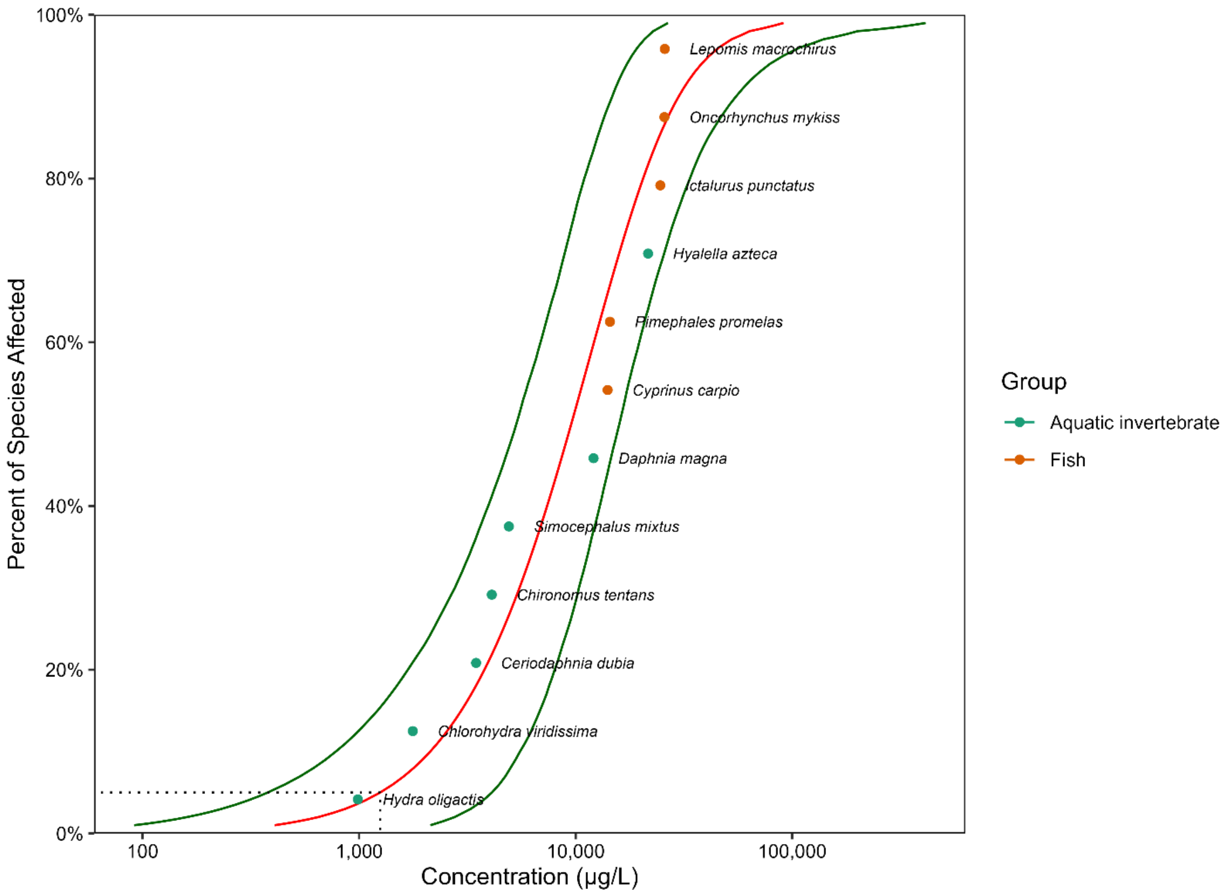

Figure 10.2. The distribution of LC_{50} estimates used to derive the antimony type A2 short-term acute water quality guideline for the protection of freshwater aquatic life.
The red line represents the fit of the averaged distribution, and the green lines represent the 95% confidence intervals of the fit. Dashed line denotes the HC_5 at the concentration of 1,250 µg/L.

There are several uncertainties that need to be considered when assigning the AF for the acute WQG. There are no data for plants or amphibians, both of which are highly desirable to include if available. Although the toxicological data suggest that aquatic species are not sensitive, further information on amphibians and plants is required to ensure the recommended WQG is in fact a low-risk benchmark for these taxa. This is especially important given that EPT taxa, a keystone aquatic group known to be sensitive to metals (Brix et al., 2011), provide essential ecological services and are a major food supply for fish in these ecosystems. Based on the considerations provided in Table 10.6 and those described above, an AF of 5 was applied to the estimated HC_5 which gave an acute short-term WQG of 250 µg/L (applied for both Sb (III) and Sb(V)).

The proposed short-term chronic WQG for Sb (Sb (III) and Sb(V)) of 250 µg/L is 100 times higher than the highest observed 90th percentile across sampling station in B.C. (Section 6.1).

Table 10.6. Considerations for determining the assessment factor for acute short-term WQGs.

Consideration	Evaluation
The taxonomic and life stage representativity of the database.	No available information on amphibians, EPT, aquatic plants or algae.
Knowledge of the toxicity modifying factors and mode of action of the substance	There is limited information on the potential toxicity modifying factors of Sb and while there is a working hypothesis for mode of action, it remains supposition (see Sections 7 and 8).
Whether or not the SSD dataset includes no effect and low effect levels and/or lethal and non-lethal endpoints.	The SSD dataset contains only lethal endpoints (i.e., LC_{50}).
Statistical uncertainties of the HC_5 estimate	The HC_5 estimation is 1250 and the lower and upper CLs of the HC_5 are 369, and 4240 respectively.
The Level of agreement between the estimated HC_5 and mesocosm and/or field studies	No information is available on mesocosm and/or field studies.

10.1.2.1 Protectiveness of B.C. acute antimony guidelines against short-term effects on survival

The WQG derivation protocol characterizes the protection of aquatic life by protecting individual organisms, resulting in the overall protection of populations (ENV, 2019). However, the most abundant effect level in short-term toxicity studies is the LC_{50} (i.e., the concentration that causes lethality of half the test population). Although the application of an AF offers further protection, acute WQGs based on LC_{50}'s may not be protective of sensitive species. To test this, the acute WQG was compared against no-effect concentrations for sensitive species.

Following B.C. protocol (ENV, 2019a), LC_{10} values for the three lowest effect concentrations are to be calculated from raw data provided in the individual studies and compared against the acute WQG. While LC_{10} values could not be calculated for the three most sensitive species because raw data were not included in the studies, the proposed WQG was compared to the LC_{50}'s in Table 10.7.

The proposed guideline of 250 µg/L was between 4 and 100 times lower than the corresponding LC_{50} values. Therefore, the recommended acute WQG of 250 µg/L should protect sensitive species against short-term effects on survival.

Table 10.7. Acute toxicity values for all species included in the short-term toxicity dataset compared to the proposed WQG of 250 µg/L.

Species	LC_{50} (ug/L)
Hydra oligactis	987
Chlorohydra viridissima	1,770
Ceriodaphnia dubia	3,470
Chironomus tentans	4,100
Simocephalus mixtus	4,920
Daphnia magna	12,100
Cyprinus carpio	14,050
Pimephales promelas	14,400
Hyalella azteca	21,600
Ictalurus punctatus	24,600
Oncorhynchus mykiss	25,700
Lepomis macrochirus	25,800

Note: Species are organized in order of most to least sensitive

10.2 Application of Water Quality Guidelines for Freshwater Aquatic Life

The Sb WQGs for the protection of freshwater aquatic life represents predicted no-effect concentrations for the most sensitive life-stage of the most sensitive species. The long-term chronic WQG represents a level which is predicted to protect all aquatic species from negative sub-lethal effects of Sb over indefinite exposures. The short-term acute guideline is designed to protect aquatic species from severe effects, such as lethality, and represents a level that should not be exceeded at any given time.

Generally, for metals, the dissolved fraction is shown to cause adverse effects and be a better representative of toxicity compared total concentration (ENV, 2019), however, this phenomenon is not demonstrated for Sb. In addition, majority of studies that tested the toxicity of Sb are used the total Sb concentration. Therefore, the recommended WQGS are based on total Sb concentration.

Antimony concentrations are variable in natural waters; therefore, an averaging period approach is used to compare environmental conditions to the WQG. Average concentrations are calculated from a minimum of five weekly samples collected over a 30-day period. Only 20% of the samples (e.g., 1 in 5 samples) can exceed the chronic Sb WQG, provided that the short-term acute WQG is never exceeded. In cases where less than five samples are available, each Sb concentration is compared individually against the chronic long-term WQG.

The Sb short-term acute WQG is a concentration that should not be exceeded at any time (both Sb (III) and Sb (V)) to meet the intended protection of the most sensitive species and life stage against severe effects. Short-term maximum WQGs are intended to assess risks associated with infrequent and transient exposure events such as spills.

The long-term chronic and short-term acute WQGs developed in this document do not allow for the direct evaluation of the toxic effects of Sb in combination with other substances (e.g., the possible synergistic or antagonistic interactions). Rather, the application of an AF is meant to account for data deficiencies and various uncertainties in extrapolating laboratory data to field conditions. Additional investigation may be needed at sites with multiple contaminants to ensure the protection of freshwater aquatic life.

11. DATA GAPS AND RESEARCH NEEDS

11.1 Freshwater Aquatic Life

More research is needed on the mechanism of toxicity and effects on more aquatic organisms to further assess the risks of Sb to freshwater aquatic life. Specifically, the following information would reduce the uncertainty of a Sb WQG for freshwater aquatic life.

- Short-term acute toxicity testing on resident amphibian and plant species
  - The short-term acute toxicity dataset lacked acceptable studies that examined the toxicity of Sb on amphibians and plant species (algal and/or vascular plants). Therefore, more studies are required that explore Sb toxicity on a more diverse range of test species that are resident to B.C.
- Toxicity testing on resident Ephemeroptera, Plecoptera and Trichoptera (i.e., EPT)
  - Ephemetoptera (mayfly), Plecoptera (stonefly), and Trichoptera (caddisfly) often represent the sensitive end of the insect community with respect to contaminant exposure (ENV, 2019; Versteeg et al., 1999). Further, there are no data for amphibians. More Sb toxicity tests with focus on these groups are required to upgrade the WQG from Type A2 to Type A1.
- Further research into toxicity modifying factors
  - There is limited information on the potential toxicity modifying factors of Sb and while there is a working hypothesis for mode of action, it remains supposition.
- Field or mesocosm studies of long-term exposures of freshwater aquatic life to elevated Sb concentrations.

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