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Updated Draft Assessment

Hydrogen Sulfide (H_2S), Sodium Sulfide ($Na(SH)$) and Sodium Sulfide (Na_2S)

Chemical Abstracts Service Registry Numbers

7783-06-4
16721-80-5
1313-82-2

Environment and Climate Change 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 hydrogen sulfide (H_2S; Chemical Abstracts Service Registry Number [CAS RN[1]] 7783-06-4), sodium sulfide (Na(SH)), referred to as sodium bisulfide in this assessment (CAS RN 16721-80-5), and sodium sulfide (Na_2S; CAS RN 1313-82-2). A draft assessment for hydrogen sulfide, sodium bisulfide, and sodium sulfide was published in September 2017. New information subsequently became available regarding incidental releases of hydrogen sulfide and exposure to humans and the environment. As a result, the draft assessment was updated.

Hydrogen sulfide is a naturally occurring inorganic gas produced from the anaerobic degradation of organic matter and is therefore widely present in anaerobic sediments and water and in biological wastes. It is found naturally in crude oil petroleum, natural gas, volcanic gases, and hot springs and is released from these natural sources primarily to air and to water under specific environmental conditions. It can also be released as a result of anthropogenic activities. Industrial operations that release hydrogen sulfide in Canada include oil and gas facilities, kraft pulp and paper mills, wastewater treatment systems, mining production, and intensive livestock operations. Hydrogen sulfide can also be released from inactive oil and gas wells in Canada.

According to information submitted in response to a CEPA section 71 survey, sodium bisulfide is used commercially as a non-pesticidal agricultural substance in non-pesticidal agricultural products, or as a dye or intermediate in paints and coatings and building and construction materials (wood and engineered wood). Sodium sulfide is used in Canada in pulp and paper processing, wastewater treatment, mining, and smelting, and may be used as a component in the manufacture of food packaging materials but with no direct contact with food. These two substances will dissociate to form bisulfide and sulfide anions and hydrogen sulfide if released to water; however, they are not expected to be released to air because of their low vapour pressure. Considering that the likely medium of release for these substances is the aquatic environment, the environmental assessment is focused on hydrogen sulfide. It has been noted that hydrogen sulfide can be released directly to air, or it can volatilize to air from other environmental media (for example, water, soil). Similarly, if the general Canadian population were to be exposed to undissociated sodium bisulfide or sodium sulfide, either salt would rapidly and completely hydrolyze in bodily fluids, resulting in the formation of hydrogen sulfide. No specific additional hazard is associated with eithersalt

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beyond that associated with hydrogen sulfide. As such, the human health risk characterization is also focused on exposure to hydrogen sulfide.

Concentrations of hydrogen sulfide have been measured in air, surface water, groundwater, and wastewater effluents in the vicinity of pulp and paper operations, oil and gas facilities, wastewater treatment systems, and livestock operations. Incidental releases of hydrogen sulfide have also been measured near inactive oil and gas wells in Ontario, Canada. There are over 279 000 inactive oil and gas wells in Canada. It is reasonable to expect that some inactive oil and gas wells in other provinces and/or territories are also producing incidental releases of hydrogen sulfide, although such data are lacking.

Hydrogen sulfide has the potential to harm both aquatic organisms and terrestrial plants when they are exposed to low concentrations. However, in the case of plants, low concentrations can also have stimulatory effects.

A risk quotient analysis determined that current ambient hydrogen sulfide concentrations in Canadian air near certain anthropogenic sources are unlikely to be high enough to cause adverse effects to terrestrial organisms (mammals or plants) and that the concentrations in surface water near potential sources are unlikely to cause adverse effects to aquatic organisms. However, information is available indicating there are also incidents of releases of high levels of hydrogen sulfide from inactive oil and gas wells. Although there are limitations to the data, the overall number of reports of incidental exposure, combined with the number of inactive oil and gas wells in Canada, indicates that these incidental releases could be a potential cause for ecological concern. Sodium bisulfide and sodium sulfide are not identified as being associated with hydrogen sulfide exposures of concern to the environment.

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

Inhalation is expected to be the predominant route of hydrogen sulfide exposure to the general population; therefore, the health effects assessment is focused on the effects by this route. Critical effects associated with hydrogen sulfide include respiratory and neurological effects. No genotoxicity or carcinogenicity classifications by other national or international regulatory agencies were identified. Available information does not indicate that hydrogen sulfide is genotoxic or carcinogenic.

Hydrogen sulfide present in ambient air comes from natural and anthropogenic sources, and a review of the available data on continuous air monitoring indicates that a representative upper-bounding range of ambient air concentrations to which the general population would be exposed is 0.001 ppm to 0.031 ppm (0.0014 mg/m^3 to 0.0434 mg/m^3). The lowest value of this range represents the overall average concentration measured in an urban area presumed to be away from major anthropogenic sources; the highest value of the range is the highest of all 99th percentile concentrations derived from measurements near point sources in Canada. Margins between upper-bounding concentrations of hydrogen sulfide in ambient air and levels associated with critical health effects (ocular, respiratory, and neurological) are considered to be adequate to address uncertainties in the health effects and exposure data used to characterize risk. These margins are also expected to account for the formation of hydrogen sulfide from the commercial uses of sodium bisulfide and sodium sulfide.

According to information received from provincial and municipal jurisdictions in Ontario, incidents of release of high levels of hydrogen sulfide from inactive oil and gas wells in Canada also occur. These incidents potentially result in acute exposure of the general population to levels approaching or exceeding concentrations of hydrogen sulfide associated with acute respiratory effects. Accordingly—although it is recognized that there are limitations associated with the nature of the data on incidental releases—given the magnitude of reported incidental concentrations, the level at which acute health effects can occur, and the number of incidents that were reported, combined with the number of inactive oil and gas wells in Canada, it is determined that there is a potential concern for human health associated with incidental exposure to hydrogen sulfide.

There are groups of individuals within the Canadian population who, due to greater susceptibility or greater exposure, may be more vulnerable to experiencing adverse health effects from exposure to substances. In the assessment of hydrogen sulfide, people living near inactive oil and gas wells who are more likely to be exposed to high levels of hydrogen sulfide from release events were considered. Additionally, data was available to account for people who have asthma and who may be more susceptible to respiratory effects from exposure to hydrogen sulfide.

Considering all the information presented in this draft assessment, it is proposed that hydrogen sulfide meets the criteria under paragraph 64(*c*) of CEPA as it is 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. It is further proposed to conclude that sodium bisulfide and sodium sulfide 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.

It is therefore proposed to conclude that hydrogen sulfide meets one or more of the criteria set out in section 64 of CEPA and that sodium bisulfide and sodium sulfide do not meet any criteria set out in section 64 of CEPA.

It is also proposed that hydrogen sulfide meets the persistence but not the bioaccumulation criteria set out in the *Persistence and Bioaccumulation Regulations* of CEPA.

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List of tables and figures

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 hydrogen sulfide (Chemical Abstracts Service Registry Number [CAS RN[2]] 7783-06-4), sodium sulfide (hereinafter referred to as sodium bisulfide; CAS RN 16721-80-5), and sodium sulfide (CAS RN 1313-82-2) to determine whether these substances present or may present a risk to the environment or to human health. These three substances were identified as priorities for assessment as they met categorization as described in ECCC, HC (modified 2017).

A draft assessment for hydrogen sulfide, sodium bisulfide, and sodium sulfide was published in September 2017. New information subsequently became available regarding incidental releases of hydrogen sulfide and potential exposure of humans and the environment. As a result, the draft assessment was updated.

This draft assessment includes the consideration of information on chemical properties, environmental fate, hazards, uses, and exposure, including additional information submitted by stakeholders. Targeted literature searches and relevant data considered for the assessment were identified up to March 2021. When available and relevant, information presented in assessments from other jurisdictions was considered. Additionally, in 2018, members of the Federal-Provincial-Territorial Committee on Health and the Environment, the Air Management Committee of the Canadian Council of the Ministers of the Environment, the Council of Chief Medical Officers of Health, and the CEPA National Advisory Committee were consulted regarding reports of incidental exposure.

Determining the ecological risk of hydrogen sulfide involves an evaluation of monitoring data from various media, including incidental releases related to inactive oil and gas wells in Canada, and analysis of hazard or fate characteristics of the substance.

The evaluation of risk to human health and assessment decisions for human health are based on considerations of data relevant to estimation of exposure of the general population. Data used include monitoring data and, in this case, reports of incidental exposure mostly related to inactive oil and gas wells, as well as information on health hazards and/or margins between conservative effect levels and

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conservative estimates of exposure. At the same time, confidence in the completeness of the identified databases on both exposure and effects is taken into account.

This draft assessment was prepared by staff in the CEPA Risk Assessment Program of Health Canada and Environment and Climate Change Canada in collaboration with the Air Health Science Division at Health Canada and incorporates input from other programs within these Departments. Measurements related to incidental releases of hydrogen sulfide were provided by the Ontario Ministry of Environment, Conservation and Parks (MOECP), and the Ministry of Natural Resources and Forestry (MNRF). These ministries were consulted on the technical portions of the assessment related to these reports of incidental releases of hydrogen sulfide.

The ecological and human health portions of this assessment have undergone external written peer review and consultation. Comments on the technical portions relevant to human health were received from scientific experts selected and directed by Toxicology Excellence for Risk Assessment, including Dr. Chris Bevan (CJB Consulting), Dr. John Christopher (California Department of Toxic Substances Control), Dr. Michael Jayjock (The LifeLine Group), and Dr. Pam Williams (E-Risk Sciences). Additionally, the first draft of this assessment, published September 2017, was subject to a 60-day public comment period. While external comments were taken into consideration, the final content and outcome of the draft 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[3], and by incorporating a weight-of-evidence approach and precaution.[4] The assessment presents the critical information and considerations upon which the proposed conclusions are based.

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[3] 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.

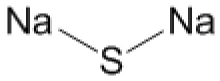
[4] A determination of whether one or more of the criteria of section 64 of CEPA are met is based upon an assessment of potential risks to the environment and/or to human health associated with exposures in the general environment. For humans, this includes, but is not limited to, exposures from ambient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

2. Identity of substances

This assessment focuses on the substance hydrogen sulfide (CAS RN 7783-06-4). Two substances that have the potential to form hydrogen sulfide in the aquatic environment, sodium bisulfide (CAS RN 16721-80-5) and sodium sulfide (CAS RN 1313-82-2), are also considered in the assessment. For this assessment, hydrogen sulfide will also be referred to as H_2S.

Information relevant to the identity of the substances is presented in Table 2-1.

Table 2-1. Substance identity

CAS RN	**DSL name** (Other names)	**Chemical formula**	**Chemical structure**	**Molecular mass** (g/mol)
7783-06-4	Hydrogen sulfide* (H_2S) (Dihydrogen sulfide)	H_2S		34.08
16721-80-5	Sodium sulfide (NaSH) (Sodium bisulfide*)	Na(SH)		56.06
1313-82-2	Sodium sulfide* (Na_2S) (Disodium monosulfide)	Na_2S		78.046

* Substance name used throughout the assessment

3. Physical and chemical properties

Hydrogen sulfide is a colourless inorganic gas that has a characteristic rotten egg odour (NRCC 1981; Budavari 1996). It is soluble in water as well as in certain polar organic solvents (Budavari 1996). It has a vapour density of 1.19 (air has a vapour density of 1.0), meaning that it will sink in air to ground level under quiet atmospheric conditions or when present in high concentrations.

Pure sodium bisulfide and sodium sulfide are both white, crystalline solids which are readily soluble in water. When exposed to water, sodium bisulfide and sodium sulfide dissociate to form hydrogen bisulfide anion (HS-) and hydrogen sulfide. When exposed to air, both substances also undergo autoxidation and gradually form polysulfur, thiosulfate, and sulfate. Sodium bisulfide also absorbs carbon dioxide, forming sodium carbonate (Bush 2000).

Concentrations in air throughout the assessment are typically presented in units of both ppm or ppb and mg/m^3 or µg/m^3. When converting between units, a ratio of 1.4 µg/m^3 = 1.0 ppb was used. These calculations were done for the purposes of this assessment, unless otherwise stated.

Table 3-1. Physical and chemical properties of hydrogen sulfide

Property	Type	Value	Temperature (°C)	Reference
Melting point (ºC)	Experimental	-85.49	N/A	Budavari 1996
Boiling point (ºC)	Experimental	-60.33	N/A	Budavari 1996
Vapour density	Experimental	1.19	15	HSDB 2003
Vapour pressure (kPa)	Experimental	562	-20	Bush 1980
Vapour pressure (kPa)	Experimental	1049	0	Bush 1980
Vapour pressure (kPa)	Experimental	1814	20	HSDB 2003
Vapour pressure (kPa)	Experimental	2026	25.5	Weast 1982
Henry's Law constant (Pa·m^3/mol)	Experimental	993 (0.0098 atm·m^3/mol)	25	HSDB 2003
Water solubility (mg/L)	Experimental	7100 5380 3980 5000	0 10 20 20	Bush 1980
pK$_a$ (dimensionless)	Experimental	7.04 pK$_a$ (1) ($H_2S \longleftrightarrow HS^-$) 11.96 pK$_a$ (2) ($HS^- \longleftrightarrow S^{2-}$)	Not provided	ATSDR 2006
Water/air conversion factors for units	N/A	1 ppm = 1.40 mg/m^3	20 (101.3 kPa)	ATSDR 2006

		1 mg/m^3 = 0.71 ppm		

Abbreviations: N/A = not applicable; pK_a = acid dissociation constant.

Table 3-2. Physical and chemical properties of sodium bisulfide and sodium sulfide

Property	Sodium bisulfide (Na(SH))	Sodium sulfide (Na_2S)
Melting point (°C)	350 (at 99.7 kPa)[a]	1180[a]
Boiling point (°C)	123[b]	NA[c]
Density	1.79 g/cm^3[c]	1.856 g/cm^3[a]
Vapour pressure (Pa)	Negligible[b]	NA
log K_{ow}	-3.5[b]	-3.5[d]
Water solubility	500 000 mg/L (at 22°C)[c]	186 000 mg/L (at 20°C)[e]

NA: not available

[a] Budavari 1996

[b] ILO 2008

[c] ECHA 2019a

[d] ILO 2012

[e] Chemical Book 2016

4. Sources and uses

4.1 Sources

Hydrogen sulfide

It has been estimated that natural sources account for 60% to 90% of the hydrogen sulfide in the atmosphere globally (US EPA 1993; Watts 2000). Hydrogen sulfide is produced naturally through non-specific and anaerobic bacterial reduction of sulfates and sulfur-containing organic compounds, such as proteins and amino acids (Hill 1973). It is also produced endogenously in humans and other mammals as part of normal biological function by the brain, liver, heart, and gastrointestinal tract (Kimura 2002; Kamoun 2004; Linden et al. 2010). It is found naturally in crude petroleum, natural gas, volcanic gases, and hot springs and is released from these natural sources primarily as a gas. Hydrogen sulfide is found naturally in a variety of environmental media—including anaerobic aquatic sediments and groundwater—owing primarily to the bacterial reduction of other forms of sulfur and methane (Dusseault et al. 2014; Chafin 1994).

Hydrogen sulfide is also emitted by some plant species as a by-product of sulfite metabolism (Takemoto et al. 1986). Some higher plants produce and release hydrogen sulfide by means of an enzymatic reaction with carbonyl sulfide (Watts 2000). Estimates of the terrestrial emission rate of hydrogen sulfide—including releases from tropical forests and other vegetation sources—can vary widely. Watts (2000), for example, estimated this value to be 0.8 million tonnes of sulfur per year, much lower than the 10 million tonne upper-bound value of Andreae and Jaeschke (1992). Estimates of the emission rate of hydrogen sulfide from oceans, including salt marshes and estuaries, are less variable, ranging from <1.5 million to 2.3 million tonnes of sulfur per year (Watts 2000; Andreae and Jaeschke 1992). Annual global releases of hydrogen sulfide from all natural sources have been estimated by Watts (2000) to be about 4.4 million tonnes, a value that is lower than some previous estimates (for example, 4.7 million to 13 million tonnes; Andreae and Jaeschke 1992).

Hydrogen sulfide can also be released as a result of agricultural activities or industrial processes. These include releases as a by-product from petroleum sector activities (Environment Canada 2004a) since natural gas and gases associated with crude oil contain hydrogen sulfide at levels varying from trace amounts to between 70% and 80% by volume (Pouliquen et al. 1989). This also includes releases during hydraulic fracturing (Marriott et al. 2016; Kahrilas et al. 2015).

Inactive oil and gas wells are also sources of hydrogen sulfide. Inactive oil and gas wells include those which are considered suspended (not producing but not decommissioned), abandoned (not producing and have been decommissioned), or orphaned (with no legally responsible and/or financially able party to deal with its abandonment and reclamation responsibilities) (Appendix A). In some instances, leakages can occur from these types of wells, caused by corrosion, improper abandonment, or damage during digging for other purposes.

There are approximately 261 000 inactive (abandoned, orphaned, or suspended) wells among the western provinces of Alberta, Saskatchewan, and British Columbia, and over 11 000 in Ontario. Appendix A includes additional information on inactive wells in Canada.

Other anthropogenic sources include liquid manure storage (Blunden and Aneja 2008; Kim et al. 2008), kraft pulp and paper mills (Teschke et al. 1999; IPCS 2003; ATSDR 2006; Janssen et al. 2009), landfills (IPCS 2003; ATSDR 2006; Kim 2006), decomposition of organic waste from wastewater treatment (Muezzinoglu 2003), and other industrial processes, such as metal refining (OMOE 2007; NPRI 2013). Releases to the environment are primarily in the form of emissions to ambient air, although sulfides (including hydrogen sulfide) may also be released to water under specific environmental conditions.

According to information submitted in response to a CEPA section 71 survey (Environment Canada 2004a), most of the hydrogen sulfide generation in Canada occurs as a by-product of the purification of “sour” natural gas and the processing, upgrading, and/or refining of bitumen and “sour” crude oil, as well as a by-product in the pulp and paper sector (kraft mills). As the companies that submitted information under section 71 were not required to indicate whether the hydrogen sulfide was manufactured intentionally or as a by-product, the term “manufacturing” here includes generation of the gas as a by-product. On the basis of the results of the section 71 survey, the total amount of hydrogen sulfide manufactured in Canada for the 2000 reporting year was estimated at approximately 8.67 million tonnes (Environment Canada 2004a).[5]

Sodium bisulfide and sodium sulfide

According to information submitted in response to a CEPA section 71 survey, a total quantity of 1 000 000 to 10 000 000 kg of sodium bisulfide was reported to have been imported into Canada in the 2011 calendar year. No consumer products were reported in Canada in that survey (Canada 2012a, 2014).[6] In the 2015 calendar year, a total quantity of 9 217 213 kg of sodium sulfides (which may include sodium bisulfide, sodium sulfide, and other sulfides of sodium) was imported into Canada (StatsCan 2015).

Information regarding the import of sodium sulfide was acquired through data obtained from the Canada Border Services Agency (CBSA; CBSA 2013). In the years 2010 to 2013, a total quantity of 100 000 to 1 000 000 kg of sodium sulfide was imported into Canada (CBSA 2013).

4.2 Uses

Hydrogen sulfide

Major uses of hydrogen sulfide internationally involve the manufacturing of elemental sulfur and sulfuric acid (ATSDR 2006). Hydrogen sulfide can also be used as a chemical intermediate in the production of dyes, rubber chemicals, pesticides, polymers, plastic additives, leather, and pharmaceuticals. Other uses include the production of heavy water in the nuclear industry, as an analytical reagent, as a disinfectant in agriculture, and as an additive in extreme-pressure lubricants and cutting oils (ATSDR 2006).

No consumer product uses were reported for hydrogen sulfide in the section 71 survey (Environment Canada 2004a). Additionally, there were no reported and/or permitted uses of hydrogen sulfide in cosmetics, natural health products, and non-prescription drugs, pesticides, food additives, or food packaging materials in Canada (personal communication, emails from the Food Directorate, Natural and Non-prescription Health Products Directorate, and Consumer and Hazardous Product Safety Directorate of Health Canada, and the Pest Management Regulatory Agency, to the Existing Substances Risk Assessment Bureau, Health Canada, dated June 2016; unreferenced).

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[5] Values reflect quantities reported in response to the survey conducted under section 71 of CEPA (Environment Canada 2004a). See survey for specific inclusions and exclusions (schedules 2 and 3).

[6] Values reflect quantities reported in response to the survey conducted under section 71 of CEPA (Environment Canada 2012a). See survey for specific inclusions and exclusions (schedules 2 and 3).

Over the past decade, endogenously produced hydrogen sulfide has been identified as a gaseous signalling molecule that plays a pivotal role in several physiological processes, such as neuromodulation, vasorelaxation, anti-inflammatory activity, and cardiac contractility (Mancardi et al. 2009; Czyzewski and Wang 2012), while alterations to the homeostasis of endogenous hydrogen sulfide can lead to various pathological conditions (Holwerda et al. 2015; Kumar and Sandhir 2018). As a result, several drug therapies have emerged to exploit the benefits of hydrogen sulfide by coupling a hydrogen sulfide-releasing moiety to a conventional drug (Rossoni et al. 2010; Wallace and Wang 2015; Zaorska et al. 2020). Thus, these products may represent a potential future source of exposure with therapeutic benefits.

Sodium bisulfide (NaSH) and sodium sulfide (Na_2S)

Sodium bisulfide is used as a primary reagent for copper-molybdenum mineral separation in Canada. Although hydrogen sulfide gas formation has been reported at a copper-molybdenum plant in British Columbia, the use of technology, scrubbers, and exhaust ventilation have eliminated detectable releases of hydrogen sulfide from the facility (Chessor and Johannsen 2006).

In Canada, sodium bisulfide is not used in cosmetics (personal communication, email from the Consumer and Hazardous Product Safety Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated April 18, 2016; unreferenced), pesticides (PMRA 2010; PMRA [modified 2013]), drugs (DPD [modified 2015]), or natural health products (LNHPD [modified 2021]), nor is it a permitted food additive (Health Canada [modified 2013]). It is not used as a component in the manufacture of food packaging materials or as a component in incidental additives used in food processing establishments (personal communication, email from Risk Management Bureau, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated May 18, 2016; unreferenced). In response to a survey issued under section 71 of CEPA, sodium bisulfide was reported to be used commercially as a non-pesticidal agricultural substance in non-pesticidal agricultural products, or as a dye or intermediate in paints and coatings, and building and construction materials (wood and engineered wood).

Sodium bisulfide is reported by the European Union to be used for the manufacture of chemicals, textiles, leather or fur, pulp, paper and paper products, metals, rubber products, and plastic products (ECHA 2019a).

Sodium sulfide, in combination with sodium hydroxide (NaOH), is used in the production of pulp (Tran and Vakkilainnen 2008). Sodium sulfide may be a component of pulping liquors, depending on the process and recovery process. White liquor is used in the first stage of the kraft process; black liquor is a waste product from this process; and green liquor is the dissolved smelt of sodium carbonate, sodium sulfide, and other compounds from the recovery boiler in the kraft process.

Under section B.14.062 [S] of the *Food and Drug Regulations*, sodium sulfide is permitted in the manufacture of gelatin or edible gelatin from processing skin, ligaments, or bones of animals (Canada [1978]). There is currently no such use of sodium sulfide reported in Canada (personal communication, email from the Food Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated May 18, 2016; unreferenced).

Sodium sulfide is included on the List of Prohibited and Restricted Cosmetic Ingredients (more commonly referred to as the Cosmetic Ingredient Hotlist or simply the Hotlist), an administrative tool that Health Canada uses to communicate to manufacturers and others that certain substances may contravene either the general prohibition found in section 16 of the *Food and Drugs Act* (FDA) or one or more provisions of the *Cosmetic Regulations*. Section 16 of the FDA states that "No person shall sell any cosmetic that has in or on it any substance that may cause injury to the health of the user." In addition, the Hotlist includes certain substances that may make it unlikely for a product to be classified as a cosmetic under the FDA (Health Canada [modified 2015]). Under the entry for alkali sulfides (lithium sulfide, potassium sulfide, and sodium sulfide), these three substances are restricted to a maximum permitted concentration of 2% as sulfur in hair removal (depilatory) products (Health Canada [modified 2015]). Currently in Canada, there are no cosmetics containing sodium sulfide as an ingredient (personal communication, email from the Consumer and Hazardous Product Safety Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated April 18, 2016; unreferenced). No consumer products containing sodium bisulfide or sodium sulfide were found in Canada.

In Canada, sodium sulfide is not a permitted food additive (Health Canada [modified 2013]), nor has it been identified as being used in pesticides (PMRA 2010; PMRA [modified 2013]), drugs (DPD [modified 2015]), or natural health products (LNHPD [modified 2014]; NHPID [modified 2015]). Sodium sulfide may be used as a component in the manufacture of food packaging materials (with no potential for direct food contact) and is not used as a component in incidental additives used in food processing establishments (personal communication, email from the Risk Management Bureau, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated May 18, 2016; unreferenced). Sodium sulfide has been identified as being used as a reaction-control agent in the production of synthetic polymers for use in chewing gum base. Dietary exposure to residues of sodium sulfide, if present in a finished chewing gum product sold in Canada, is expected to be minimal (personal communication, email from the Food Directorate, Health Canada, to the Existing Substances Risk Assessment Bureau, Health Canada, dated June 16, 2016; unreferenced). Overall, exposure to sodium sulfide from food, if any, is expected to be minimal.

In terms of information on usage from outside of Canada, sodium bisulfide is used as a flotation agent in mining and metal extraction, kraft pulping, dyestuff processing, hair removal from hides, rayon and cellophane desulfurizing, bleaching, the textile industry, photography engraving and lithography, and as an intermediate in the manufacture of other chemicals (SDS 2013; NICNAS 2006, 2016). Sodium sulfide is used as an active constituent in pesticides and veterinary medicines, in the treatment of hides for the manufacture of gelatin and collagen, in depilatory products, in the textile industry, in photography engraving and lithography, in heavy metal removal for wastewater treatment, and as an intermediate in the manufacture of other chemicals (NICNAS 2006, 2016). All of these international uses are industrial or commercial only (often site-limited), except for use in depilatory products (NICNAS 2016). It is also used in the production of rubber chemicals, sulfur dyes, and other chemical compounds.

Sodium bisulfide is also used in a number of products, such as pH regulators, water treatment products and water treatment chemicals, and in the manufacture of intermediates.

Sodium sulfide is used in the formulation of mixtures and/or re-packaging and municipal supply (for example, electricity, steam, gas, and water) and wastewater treatment, including the manufacture of chemicals, textile, leather or fur, pulp, paper and paper products, rubber products, plastic products, and metals (ECHA 2019a).

5. Releases to the environment

This assessment focuses on releases of hydrogen sulfide. Sodium bisulfide and sodium sulfide are not expected to be released to air because of their low vapour pressure. In aerobic environments, the dissolved sulfide will be oxidized to sulfate. In anaerobic environments, no oxidation will occur, and the formation of hydrogen sulfide is expected. In anaerobic environments, the dissolved sulfide may precipitate with metals. Under typical surface water conditions, sodium bisulfide and sodium sulfide are expected to rapidly dissociate into hydrogen bisulfide anion (HS^-) and hydrogen sulfide. However, the exact formation quantity of hydrogen sulfide generated from sodium bisulfide and sodium sulfide is unknown and is subject to local conditions. Under very acidic conditions (pH 1.5–3.5), the formation of hydrogen sulfide will predominate.

Many industrial sectors in Canada, including the oil and gas sector, pulp and paper sector (kraft mills), livestock operations, non-metallic mineral products industries, primary metal industries and other manufacturing industries, and the waste and wastewater sector, release quantities of hydrogen sulfide, mostly to air but also to water. According to information submitted in response to a CEPA section 71 survey (Environment Canada 2004a), the pattern of hydrogen sulfide releases in Canada is similar to that reported elsewhere (IPCS 1981; Budavari 1996; Canada 2001; IPCS 2003; US EPA 2003).

Data reported to the National Pollutant Release Inventory (NPRI) indicate that the three most significant industries contributing to hydrogen sulfide air emissions in Canada have been the oil and gas, pulp and paper, and iron and steel sectors. However, in recent years, as a result of emission reductions from the pulp and paper, and iron and steel sectors, the oil and gas sector has become a relatively larger contributor to the total emissions (NPRI 2019).

According to the NPRI (2019), 148 facilities reported on-site releases of hydrogen sulfide totalling 1619 tonnes in 2017. Of those, 1519 tonnes were released to air and 100 tonnes were released to water, but there were no reported releases to land. The total amounts of hydrogen sulfide disposed of at on-site and off-site locations in 2017 were 112 407 tonnes and 36 885 tonnes, respectively. All of the hydrogen sulfide that was reported to the NPRI as disposed of on-site was injected underground. Underground injection is a regulated waste disposal method in which materials are injected into deep underground wells. A total of 20 tonnes was sent to off-site recycling in 2017. Overall, industrial releases of hydrogen sulfide in Canada decreased from 6129 tonnes in 2000 to 1619 tonnes in 2017, although reported releases to water increased from 39 tonnes reported in 2000 to 100 tonnes in 2017. This is due to an increased number of reporters rather than an increase in release quantities from individual reporters (NPRI 2019). The NPRI values reported here likely underestimate total releases from anthropogenic point sources in Canada since some significant sources are not covered by the NPRI (including intensive livestock operations, smaller upstream oil and gas facilities, and inactive oil and gas wells).

Sodium bisulfide and sodium sulfide

Sodium bisulfide and sodium sulfide are not expected to be released to air because of their low vapour pressure. Release of sodium bisulfide to the environment is likely to occur from industrial use as a processing aid, manufacturing of the substance itself, as an intermediate step in further manufacturing of another substance (use of intermediates), in the manufacture of thermoplastics, as a processing aid, and in the formulation of mixtures (ECHA 2019a).

Considering current uses, the aquatic environment is the likely medium for release of sodium bisulfide and sodium sulfide. Commercial activities involving sodium bisulfide and sodium sulfide may also form hydrogen sulfide. In the case of the two sodium salts, the anions of their dissociation (namely the bisulfide and sulfide) may be in equilibrium with hydrogen sulfide and thus indirectly result in its formation.

Sodium bisulfide is expected to react with oxygen and carbon dioxide gas in air to form sodium thiosulfate, sodium sulfite, and sodium carbonate.

5.1 Oil and gas

The amounts of hydrogen sulfide released to air by the Canadian oil and gas sector as reported to the NPRI for 2014 and 2017 were 1140 tonnes and 504 tonnes, respectively (NPRI 2019). Included in this category are upstream (that is, exploration and production) activities related to oil and gas, oil sands and heavy oil, as well as oil and gas storage and pipeline transport, and coal manufacturing activities. For 2017, the oil and gas sector reported 112 273 tonnes and 36 878 tonnes of on-site and off-site disposals for hydrogen sulfide, respectively (NPRI 2019).

The vast majority of hydrogen sulfide produced from oil sands processes and the high-concentration gas fields of British Columbia, Alberta, and Saskatchewan is burned in flare stacks, burned as a fuel, pumped back underground, or turned into elemental sulfur and sold as a product.

An inventory of greenhouse gases, criteria air contaminants, and hydrogen sulfide emissions conducted for the Canadian upstream oil and gas sector for the 2000 reporting year identified roughly 10 000 tonnes of hydrogen sulfide released (Clearstone 2004). This value, which represents about 250 facilities in Alberta, is much larger than the approximately 1500 tonnes reported to the NPRI (representing only 148 reporting facilities) by the upstream oil and gas sector in 2000 (Clearstone 2004). Most releases from these sources are not reported to the NPRI as these operations typically do not meet the reporting criteria. NPRI reporting depends on a number of criteria, including number of employees, type of facility, and quantity of substance that is manufactured, processed or otherwise used (NPRI 2019). The 2005 inventory of air contaminants was updated in 2011 (Clearstone 2014). The amount of direct hydrogen sulfide emissions in 2011 was estimated to be 3700 tonnes (uncertainty of -10.0 to +28.8%). Approximately 80% of these emissions were from natural gas production and processing, with the remainder coming from oil production. Although the release of hydrogen sulfide to the atmosphere is regulated (Clearstone 2014), some emissions occur within regulatory limits.

Under Alberta's *Oil Sands Conservation Act*, operators may not release gas containing hydrogen sulfide directly to the atmosphere. Gas from various sources, such as flare lines, relief valves, and wells, must be captured and incinerated such that essentially all of the hydrogen sulfide is converted to sulfur dioxide prior to release. Operators must also have emergency response plans in place to deal effectively with any uncontrolled releases of hydrogen sulfide. The decrease in emissions between 2005 and 2011 is reported to be primarily due to industry reductions of fugitive emissions and compressor seal venting. In 2011, the majority of hydrogen sulfide releases reported were due to fugitive equipment leaks (48%), incomplete combustion of fuels and waste gas streams containing hydrogen sulfide (31%), evaporation losses during product storage and handling (12%), and venting of waste gas streams containing low concentrations (for example, less than 10 ppm) of hydrogen sulfide (9%). The decrease in emissions from 6000 tonnes in 2005 to 3700 tonnes in 2011 is reported to be primarily due to the implementation of best management practices specified in the Alberta Energy Regulator (AER) Directive 060, which sets out requirements for flaring, incinerating, and venting in Alberta at all upstream petroleum industry wells and facilities.

A significant issue associated with the disposal of unwanted hydrogen sulfide from oil and gas facilities is the efficiencies of flares. Clearstone (2004) estimated that in 2000, 898 tonnes of hydrogen sulfide were released as result of flaring during gas processing. Estimates of flare efficiency vary, ranging from 20% to 99% (University of Alberta 2007). In Alberta, the combined volume of flared and vented solution gas is reported to have decreased by 51% from 1999 to 2008 (Johnson and Coderre 2011). Solution gases are released when crude oil is reduced from reservoir to atmospheric pressure.

It is not currently possible to reliably estimate the amounts of hydrogen sulfide being flared and vented at solution gas batteries in Alberta (Johnson and Coderre 2011). A qualitative estimate of the proportions of sweet (<10 ppm hydrogen sulfide) and sour (>10 ppm hydrogen sulfide) battery sites and gas volumes was made using Alberta Energy Utilities Board (AEUB) site inspection data. On the basis of these data, and correlating with the volumes of gas flared at individual sites, it is estimated that 36% of the gas flared and vented in the province is sour. The petroleum industry in Alberta achieved a 95.6% solution gas conservation rate in 2014, compared with 95.3% in 2013. However, since efficiencies vary considerably, the solution gas conservation rate may be considered essentially unchanged from one year to the next. Gas conservation is the recovery of solution gas to be used as fuel for production facilities, to sell, to inject for enhanced recovery from oil or condensate pools, or to generate power, among other uses (AER 2016).

No releases of hydrogen sulfide to surface water or land have been reported to the NPRI by any of the oil sands mine operators. Hydrogen sulfide is present in crude oil and may be generated in the process-affected water during open-pit mining and hot water extraction, and then transferred to tailings ponds. It may also be produced in tailings ponds from anaerobic bacterial degradation of organic compounds or by the reduction of sulfate ions added to tailings to promote their consolidation (Holowenko et al. 2000). A no-discharge policy exists for the process-affected water from open-pit mining; however, hydrogen sulfide in process-affected water can still potentially enter waterways through underground seepage from tailings ponds to groundwater aquifers that are connected to surface waters (Timoney and Lee 2009). Thus, there is a potential for indirect release of contaminants (including hydrogen sulfide) to northern Alberta rivers (RSC 2010).

Several oil sands facilities have reported hydrogen sulfide releases to air from fugitive and other non-point source releases to NPRI (2019). One mine operator reported that a small portion of hydrogen sulfide in the form of total reduced sulfur (TRS) emissions to air would be emitted from tailings ponds (RSC 2010).

Hydrogen sulfide can also be released from abandoned oil and gas wells or other inactive oil and gas wells (Jackson et al. 2020a). Release may occur into the atmosphere or into shallow groundwater from orphan wells across Canada, including Alberta, Ontario, Quebec, New Brunswick, Nova Scotia, and southwestern Newfoundland (Jackson et al. 2020b).

5.2 Pulp and paper

Hydrogen sulfide may be released to air and water from pulp and paper mills that use a kraft pulping process. Hydrogen sulfide is measured and regulated by the provinces (Alberta, British Columbia, New Brunswick, Nova Scotia, Ontario, and Quebec) as total reduced sulfur (TRS). TRS may include hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, carbon disulfide, carbonyl sulfide, and other organic compounds containing sulfur in a reduced state.

Effluent release of hydrogen sulfide from pulp and paper facilities is regulated by all of the provinces. Additionally, in order to comply with the federal *Pulp and Paper Effluent Regulations*, all kraft pulp and paper mills that discharge effluent to the environment have secondary wastewater treatment, which is expected to limit concentrations of hydrogen sulfide in the final effluent released.

NPRI data for 2017 indicate that kraft mills reported total releases of 708 tonnes of hydrogen sulfide from 21 mills across Canada (NPRI 2019). Thirteen of those mills reported a total of 77 tonnes released to water (ranging from <0.1 tonnes to 23 tonnes each), and 21 mills reported a total of 631 tonnes released to air. Less than 1 tonne was disposed of on site. These NPRI results can be divided by annual effluent volumes to generate estimates of environmental concentration. While basic corrections for metal-sulfide complexation and representative pH may be applied to these estimates, other aspects of the environmental behaviour of hydrogen sulfide cannot readily be accounted for, namely evaporation and oxidation reactions (as discussed in the Environmental Fate and Behaviour section). These phenomena are inherently addressed by monitoring data and are thus taken into account for the other sectors considered in this assessment. Therefore, available monitoring data for pulp and paper mills will be used to derive predicted environmental concentrations.

The total quantity of hydrogen sulfide releases reported in 2000 was 1926 tonnes from 34 facilities, the vast majority of which was to air. The amount of hydrogen sulfide released in 2014 was 2060 tonnes to air and 94 tonnes to water from 146 reporting facilities (NPRI 2013). Declining trends in hydrogen sulfide air emissions from the pulp and paper sector since 2001 are primarily attributed to mill closures, decreased production levels, and changes in estimation methods (NPRI 2013).

5.3 Iron and steel

According to data reported to the NPRI (2019), four integrated mills (located in Ontario) belonging to the iron and steel sector released 131.0 tonnes of hydrogen sulfide to air in 2017; 261 tonnes were released to air in 2004, 200 tonnes in 2008, 118 tonnes in 2014, and 130 tonnes in 2015.

5.4 Livestock operations

Intensive livestock operations are another source of hydrogen sulfide in Canada. Releases from these sources are not reported to the NPRI, as these operations typically do not meet the reporting criteria. Emission rates of hydrogen sulfide vary depending on local conditions and methods of manure management. The magnitude of emissions from manures is a function of liquid phase concentration, temperature, and pH. Under anaerobic conditions, livestock and poultry manures will be acidic, with pH values ranging from 5.5 to 6.5, and warm due to bacterial action. This situation creates a considerable amount of hydrogen sulfide that will rapidly come out of solution when the liquid manure is agitated or disturbed. Manure storage tanks, ponds, non-aerated lagoons, and land application sites are primary sources of hydrogen sulfide emissions.

The factors that increase the emission of hydrogen sulfide include wet manure handling at a manure pH of less than 7.0, a high temperature, and a long manure storage time. Under aerobic conditions, any reduced sulfur compounds in manure will be oxidized microbially to non-volatile sulfate, with minimal emissions of hydrogen sulfide (US EPA 2001). Hydrogen sulfide generated in dry manure is generally oxidized as diffusion through aerobic layers occurs. Confinement facilities with manure flushing systems that use fluids from anaerobic lagoons also are sources of hydrogen sulfide emissions. Runoff of hydrogen sulfide from land application of manure does not seem to be a problem at ambient temperatures, due to its tendency to evaporate and oxidize rapidly (US EPA 2001).

The quantity of hydrogen sulfide generated by intensive livestock operations has been estimated on the basis of the number of swine and cattle in Canada and an average emission factor per animal. Hydrogen sulfide production in 2001 was estimated at 126 107 tonnes, of which 121 441 tonnes came from swine and the rest from cattle (Chetner et al. 2001; Statistics Canada 2003). If proper manure management practices are followed in intensive livestock operations, hydrogen sulfide from manure application to land will be incorporated into the soil using techniques that minimize evaporative losses.

5.5 Publicly owned wastewater treatment

In 2017, the five wastewater treatment systems that reported to the NPRI (2019)—Greater Vancouver (two systems, Delta and Richmond) and Kamloops, British Columbia; Regina, Saskatchewan; and Mississauga, Ontario—indicated total on-site releases of 30.6 tonnes of hydrogen sulfide. Of this amount, 8.8 tonnes were released to air and 21.8 tonnes were released to water. In 2015, three reporting wastewater treatment systems in Canada (Regina, Kamloops, and Mississauga) released 156 tonnes to air and 0 tonnes to water (NPRI 2017). NPRI results from 2014 indicated that four wastewater treatment systems released 153 tonnes to air and 22 tonnes to water.

During prolonged periods of hypoxia, stormwater retention ponds are capable of generating hydrogen sulfide gas (d’Aoust et al. 2017; Ku et al. 2015) and, as such, may be a source of hydrogen sulfide to the environment. Water quality constituents and bacterial communities in sediment were analyzed by d’Aoust et al. (2017) in two stormwater retention ponds in Ottawa, Ontario, over a period of two years. They found that ice cover and hypoxic conditions together resulted in high hydrogen sulfide production (up to 20.7 mg/L total sulfides in water) during the winter. These high concentrations were associated with dissolved oxygen levels of less than 2 mg/L. Ku et al. (2015) also found concentrations ranging from 1.4 mg/L to 3.6 mg/L total sulfides in a stormwater retention pond in Edmonton, Alberta.

6. Environmental fate and behaviour

A summary of the physical and chemical properties of hydrogen sulfide, sodium bisulfide, and sodium sulfide that are relevant to their environmental fate are presented in Tables 3-1 and 3-2. Information on their behaviour in the environment, including their persistence and bioaccumulation potential, are presented below.

Hydrogen sulfide is a weak acid; it equilibrates with its anions HS^- and S^{2-} in aqueous solution (second and third equilibria of equation 1) (Li and Lancaster 2013).

$$H_2S(g) \rightleftharpoons H_2S(aq) \rightleftharpoons HS^- + H^+ \rightleftharpoons S^{2-} + 2H^+ \quad \text{Equation 1}$$

Based on equation 1, the leftward equilibrium shift could cause a decrease in hydrogen sulfide concentration but also an increase of the solution pH. Equation 1 is also the basis of the application of hydrogen sulfide gas or inorganic metallic sulfide, such as sodium sulfide (Na_2S) and sodium bisulfide (NaSH) as hydrogen sulfide sources in solution. An unbuffered stock solution from hydrogen sulfide gas tends to be acidic, whereas that from metallic sulfide is basic (Li and Lancaster 2013).

Sodium bisulfide and sodium sulfide

When exposed to air, sodium bisulfide undergoes autoxidation and gradually forms polysulfur, thiosulfate, and sulfate. It also absorbs carbon dioxide, forming sodium carbonate (Bush 2000). Sodium sulfide, when exposed to air, will oxidize to sodium sulfate (Na_2SO_4), although a number of intermediate sulfur compounds (polysulfides and thiosulfates) will also result (HIGP 1989). Sodium bisulfide is very soluble in water. In this medium, the substance will immediately dissociate; the sulfur will enter the natural sulfur cycle and, depending on the pH, hydrogen sulfide can form. Sodium sulfide is a solid under environmental conditions, with a high boiling point and high water solubility. The substance is readily soluble in water.

6.1 Environmental distribution and persistence

Hydrogen sulfide is expected to be released to the environment through air and water. Hydrogen sulfide is a gas under environmental conditions and is expected to partition from water or land into the atmosphere. The substance's atmospheric residence time ranges from 0.6 to 29 days. Hydrogen sulfide is soluble in water and is mobile in aquatic environments and moist soil; its aquatic aerobic half-life is short.

6.1.1 Air

Hydrogen sulfide is a gas under typical environmental conditions, so when it is released to water or land, it tends to partition from these media into the atmosphere. Hydrogen sulfide that is released into the atmosphere may form localized, low-lying clouds that are rapidly dispersed and consequently diluted by windy conditions and turbulence

(NRCC 1981). This dispersion may be accompanied by wet deposition, dry deposition, and chemical transformations, which further decrease ambient concentrations.

Hydrogen sulfide does not absorb solar radiation in the lower atmosphere (troposphere) and thus is photochemically stable (Warnek 1988).

Hydrogen sulfide is removed from the atmosphere mainly by oxidation reactions with hydroxyl radicals (OH•). The rate constant for the reaction of hydroxyl radical with hydrogen sulfide has been experimentally determined to be $(5.2 \pm 0.8) \times 10^{-12}$ cm^3/s (Barnes et al. 1986).

The residence time of hydrogen sulfide in the atmosphere is affected by location, temperature, and other atmospheric variables, such as concentrations of radical precursors, sunlight, and humidity. The mean tropospheric conversion time of hydrogen sulfide to sulfur dioxide by reaction with hydroxyl radicals in California is about 18 hours (Sprung 1977; NRCC 1981). Jaeschke et al. (1980) found a significant maximum concentration in winter and a minimum concentration in summer. The atmospheric residence time of hydrogen sulfide has been estimated to range from 0.93 days in summer to 42 days in winter at a latitude equal to that of Edmonton, Alberta (Bottenheim and Strausz 1980), equating to atmospheric half-lives of approximately 0.65 and 29 days, respectively. This variation is due in part to the thermal sensitivity of the chemical transformations of hydrogen sulfide, with decreased temperatures and sunlight as well as decreased levels of hydroxide radicals in northern regions tending to slow reaction rates. In many places in Canada, the atmospheric half-life of hydrogen sulfide is thus expected to be significantly greater than two days during most of the winter months.

6.1.2 Surface water and soil

Hydrogen sulfide is a gas that is quite soluble in water, which makes it highly mobile in moist soils and aquatic environments. Several species of soil and aquatic microorganisms oxidize hydrogen sulfide to elemental sulfur (S^0) under aerobic conditions, and its degradation half-life in these environments usually ranges from one to several hours (Jørgensen 1982). Volatilization is also an important loss mechanism from soils. However, soils can also act as a sink for airborne hydrogen sulfide being adsorbed onto clay or organic matter, followed by rapid chemical and biological oxidation to elemental sulfur (Cihacek and Bremner 1993). A number of organisms have been found to degrade hydrogen sulfide to elemental sulfur and sulfate, including a heterotrophic bacterium isolated from dimethyldisulfide-acclimated peat (Cho et al. 1992), heterotrophic fungi (Phae and Shoda 1991), and the marine isopod *Saduria (Mesidotea) entomon* (Vismann 1991).

Because of its physical and chemical properties and fate, hydrogen sulfide is very short-lived in water under aerobic (oxic) conditions. Hydrogen sulfide will evaporate relatively rapidly from water, depending on factors such as temperature, humidity, and pH (HSDB 2003). The environmental model WVOLWIN uses a Henry's Law constant value to predict an aquatic evaporative half-life of 38 minutes in a river and 56 hours in a lake (Environment Canada 2002). The model does not, however, take into account the fact that a portion of dissolved hydrogen sulfide is ionized. Actual half-lives could therefore be somewhat longer, especially in alkaline water where the dominant species is the HS^- ion. Although the oxidative half-life of hydrogen sulfide in water and wastewater is typically also quite short (that is, hours to minutes; for example, Millero et al. 1987; Nielsen et al. 2007; Palumbo et al. 2010), rates are difficult to predict with accuracy due to the complexity of the reactions involved. Sulfides can react chemically with dissolved oxygen, but this is thought to be a slow and complex chain reaction (Millero et al. 1987; Kotronarou and Hoffmann 1991; Nielsen et al. 2003). General rate equations have been developed for wastewater (Wilmot et al. 1988; Nielsen et al. 2004) and pulp and paper mill (Palumbo et al. 2010) effluent, but they do not account for all of the significant factors involved in the oxidation of hydrogen sulfide. In general, in aerobic water oxidation rates can vary (by a factor of up to 100) depending on concentrations of dissolved metals (for example, nickel, cobalt, manganese, and copper), temperature, concentration of other reactants, pH, amount and type of microbial activity, and ionic strength. In addition, the presence of some commonly found organic chemicals in wastewater can increase or decrease the oxidation rate.

However, hydrogen sulfide can exist for relatively long periods in water under anoxic conditions and is often associated with anoxic sediments (Andreae and Jaeschke 1992).

When hydrogen sulfide enters oxygenated water, it dissolves and dissociates to form an equilibrium between un-ionized hydrogen sulfide, bisulfide ions HS^-, and sulfide ions S^{2-}.

Dissociation in water depends primarily on the pH of the water, although temperature and ionic strength of the solution have an effect as well (Holm et al. 2000). The dominant species will be hydrogen sulfide and the bisulfide anion. As the pH increases, the ratio of the concentration of bisulfide ion to aqueous hydrogen sulfide increases. At pH 6.0 and a temperature of about 20ºC, 91% will be un-ionized hydrogen sulfide, decreasing to about 9% at pH 8.0 (Pomeroy and Boon 1990; Table 8-1). Natural variations in water pH can therefore have a significant effect on the proportion of hydrogen sulfide present. Temperature variations have a more limited influence on the extent of ionization, with lower temperatures favouring the un-ionized hydrogen sulfide form. For example, at a pH of 7.0, the proportion of un-ionized hydrogen sulfide present increases from approximately 50% to 60% as the temperature drops from 20ºC to 10ºC (Australia and New Zealand Environment and Conservation Council 2000).

Table 6-1. Proportions of dissolved sulfide present as un-ionized hydrogen sulfide and as HS- at environmentally relevant pH and a temperature of approximately 20ºC (from Pomeroy and Boon 1990)

pH	Proportion of un-ionized H_2S	Proportion of HS^-
5.0	0.99	0.01
6.0	0.91	0.09
6.2	0.86	0.14
6.4	0.80	0.20
6.6	0.72	0.28
6.8	0.61	0.39
7.0	0.50	0.50
7.2	0.39	0.61
7.4	0.28	0.72
7.6	0.20	0.80
7.8	0.14	0.86
8.0	0.09	0.91
8.2	0.059	0.941
8.4	0.039	0.961
8.6	0.025	0.975
8.8	0.016	0.986
9.0	0.010	0.99

When free H_2S/HS^- is introduced into either aerobic or anaerobic fresh water containing metals, reactions with dissolved iron and other metals are expected to occur, producing dissolved metal (principally iron) sulfide complexes, which may precipitate out of solution if concentrations are high enough. Reactions of this type are expected, for example, in anoxic sediments (Luther et al. 2003). Rozan et al. (2000) have suggested that the relatively large quantities of dissolved iron sulfide complexes found by them in oxic river water in the northeastern United States had diffused upwards into the water column from underlying anoxic sediments.

6.2 Potential for bioaccumulation

No reliable bioaccumulation data were identified for hydrogen sulfide. However, bioconcentration and food chain biomagnification of hydrogen sulfide are unlikely, considering that it is an inorganic gas and has a relatively short half-life in water. Because hydrogen sulfide is an inorganic gas, it is not expected to bioconcentrate or bioaccumulate.

Sodium bisulfide and sodium sulfide oxidize in air, are soluble in water, and, given their respective log K_{ow}s (<-3.5 for both), neither substance is expected to bioconcentrate in the environment (ILO 2002, 2008).

7. Potential to cause ecological harm

7.1 Ecological effects assessment

Empirical data on the effects of hydrogen sulfide were considered in the weight-of-evidence for assessing the ecological effects of hydrogen sulfide. Although the three charge states occur naturally in the environment (H_2S, HS^-, and S^{2-}), it is unlikely that HS^- will diffuse easily into cells, because it is charged. In contrast, hydrogen sulfide is more capable of permeating cell membranes (Powell 1989).

Limited information has been identified on the ecological toxicity of sodium sulfide and sodium bisulfide. Sodium sulfide and sodium bisulfide are unstable in water and, at pH 7.0, will dissociate into hydrogen bisulfide anion (HS-) and hydrogen sulfide. Under acidic conditions, the formation of hydrogen sulfide will predominate. Therefore, the toxicity of sodium sulfide and sodium bisulfide will focus on hydrogen sulfide. Available ecological toxicity information for sodium bisulfide and sodium sulfide is reported as read-across from hydrogen sulfide.

7.1.1 Mode/mechanism of action

In wildlife (crustaceans, algae, fish, and other vertebrates), hydrogen sulfide is considered to have a reactive mode of action. Notably, it has been proposed that toxicity is primarily due to the immediate binding of hydrogen sulfide to the enzyme cytochrome-c-oxidase or other metallo- and disulfide-containing proteins (Beauchamp et al. 1984; Dorman et al. 2002). Others have hypothesized the un-coupling of mitochondrial respiration via the opening of the mitochondrial permeability transition pore to be an additional mechanism of toxicity, resulting in the depletion of intracellular levels of adenosine triphosphate (Thompson et al. 2003). Hydrogen sulfide is a potent inhibitor of the cytochrome oxidase system and thus inhibits oxidative phosphorylation, leading to cellular asphyxia. Because the primary mechanism is inhibition of aerobic mitochondrial respiration and occurs rapidly, the potential for longer-term chronic impacts is minimal (Weston Solutions Inc. 2006). In plants, hydrogen sulfide has been shown to inhibit oxygen release (Joshi et al. 1975).

7.1.2 Effects on aquatic organisms

Hydrogen sulfide has been demonstrated to have harmful effects on aquatic organisms at low concentrations.

For a given measured concentration of free dissolved sulfide (excluding dissolved metal sulfides), exposure of aquatic organisms to un-ionized hydrogen sulfide is highly dependent on water pH and, to a lesser degree, on temperature.

As indicated earlier in Table 3-1, at a pH of 5.0 and a temperature of about 20°C, about 99% of the sulfide is present as un-ionized hydrogen sulfide; at a pH of 8.0, about 91% is in the form of HS^-.

The toxicity of dissolved sulfides is typically believed to derive primarily from exposure to un-ionized hydrogen sulfide rather than to the bisulfide ion, HS^- (US EPA 1976). As temperature increases, the degree of toxicity also increases, likely due to the increased metabolic demands in ectothermic aquatic organisms (Broderius and Smith 1976). However, Broderius and Smith (1976) reported that the toxicity of un-ionized hydrogen sulfide to fathead minnow appeared to increase over the pH range of 6.5 to 8.7. Nevertheless, the overall magnitude of this effect was relatively small, resulting in an approximately two-fold decrease of LC_{50} values (that is, concentration expected to cause mortality in 50% of test animals) over the pH range of 7.5 to 8.5. These results suggest that the HS^- ion, concentrations of which increased as the pH of the test waters was increased, was responsible for some of the observed toxicity. An alternative explanation offered by the authors posited that, since the actual pH at the gill surfaces of fish is substantially lower than the measured ambient levels, fish would be exposed to a higher proportion of un-ionized hydrogen sulfide than was predicted on the basis of measured pHs, particularly under more alkaline conditions. The other possibility—that the HS^- ion itself contributed to the toxic response—is supported by evidence of the uptake of HS^- by some aquatic organisms (Julian and Arp 1992; Czyzewski and Wang 2012)

Available acute, chronic, and early life-stage toxicity data for aquatic organisms are summarized in US EPA (2009). A selection of data from this source is presented in Table 7-1. All data are reported as concentrations of un-ionized hydrogen sulfide. The following brief description of the data is based on information presented in US EPA (2009).

Acute toxicity values for freshwater fish (7 values) and invertebrates (9 values) range from 2.0 µg/L to 1070 µg/L, while acute values for estuarine/marine fish (1 value) and invertebrates (7 values) range from 10 µg/L to 1430 µg/L. Chronic toxicity data are mostly available for freshwater organisms, with values for fish (14 values), invertebrates (6 values), and algae (1 value) ranging from 0.5 µg/L to 1874.4 µg/L. Early life-stage toxicity data (48 values) are mostly available for short-term tests with freshwater organisms, with various measures of effects on fish and invertebrates reported at concentrations ranging from <2 µg/L to 2900 µg/L. The no-observed effect concentration (NOEC) in freshwater fish was 0.4 µg/L for swimming endurance in adult bluegill (*Lepomis macrochirus*) over 97 days (US EPA 1976). The difference between the acute and chronic effect concentrations is small and may be due to the mode of action of hydrogen sulfide. Hydrogen sulfide paralyzes the brain and metabolic functions controlling respiration.

Of the 91 toxicity results included in US EPA (2009), effects on four different freshwater species and one marine species are reported at concentrations of 2 µg/L or below, and over 20 effect values representing 10 different species, mostly freshwater, are reported in the 2 µg/L to 10 µg/L range.

Regarding the lowest effect values, Fung and Bewick (1980) reported a 96-hour LC_{50} of 2.0 µg/L and <2.0 µg/L for sac fry of whitefish (*Coregonus clupeaformis*) and yellow perch (*Perca flavescens*), respectively. Smith et al. (1976) reported a 97-day lowest-observed-effect concentration (LOEC; reproduction) of 1 µg/L for bluegill *(Lepomis macrochirus*). Thompson et al. (1991) reported a 49-day LOEC (decreased weight) of 1.1 µg/L for sea urchin (*Lytechinus pictus*). Lastly, Hoque et al. (1998) reported a 6-week LOEC (reduced growth) of 0.5 µg/L for the freshwater tropical fish *Mystus nemurus*.

Results of a recent review of the aquatic toxicity focused on marine biota (Weston Solutions Inc. 2006) suggest that marine organisms are generally less sensitive to hydrogen sulfide than freshwater organisms. The lowest mean species effect values reported in this review were a LOEC of 11.1 µg/L for the mysid shrimp (*Americamysis bahia*) and an EC_{50} (that is, concentration expected to cause a specified adverse effect in 50% of test animals) of 7.6 µg/L for the larval bay mussel (*Mytilus galoprovincialis*). The authors of this study further determined that hydrogen sulfide typically acts in an acutely toxic manner regardless of the test exposure period and that, consequently, it is appropriate to combine short- and longer-term aquatic effects data when estimating a toxicity threshold.

A critical toxicity value (CTV) of 1.0 µg/L has been selected for determining a predicted no-effect concentration (PNEC) for use in the assessment of toxicity to freshwater aquatic organisms. The bluegill (*Lepomis macrochirus*) sac fry was selected as the most sensitive organism on the basis of a LOEC of 1 µg/L and from a review of both acute and chronic studies.

Sodium bisulfide and sodium sulfide

Limited data on acute and chronic aquatic toxicity are available for the precursors, sodium bisulfide and sodium sulfide. All results utilize read-across data from hydrogen sulfide or sodium sulfide nonahydrate (CAS RN 1313-84-4).

Table 7-1. Selection of aquatic toxicity data for hydrogen sulfide[a]

Species	Duration and Test Endpoint	pH During Test[b]	Value (µg/L)	Reference
Microalgae (*Scenedesmus vacuolatus*)	24-hour EC_{50}	6.5–6.6	1874.4	Küster et al. 2005
Isopod (*Asellus militaris*)	96-hour LC_{50}	7.5	1070	Oseid and Smith 1974; US EPA 1976
Ephemeroptera (*Baetis vagans*)	96-hour LC_{50}	7.6	20.0	Oseid and Smith 1974; US EPA 1976
Giant mayfly (*Hexaqenia limbata*)	96-hour LC_{50}	7.7	111.0	Oseid and Smith 1974

Species	**Duration and Test Endpoint**	**pH During Test**[b]	**Value (µg/L)**	**Reference**
Crustacean (*Daphnia magna*)	48-hour EC_{50}	6.4–6.5	122.0	Küster et al. 2005
Fathead minnow (*Pimephales promelas*)	96-hour LC_{50}	7.9	16.0	US EPA 1976
White sucker (*Catostomus commersonii*)	96-hour LC_{50}	7.8	18.5	US EPA 1976
Bluegill (*Lepomis macrochirus*)	96-hour LC_{50}	7.8–8.0	44.8	Smith et al. 1976
Fathead minnow (*Pimephelas promelas*) – fry	96-hour LC_{50}	7.9	6.6	US EPA 1976
Rainbow trout (*Salmo gairdneri*) – juvenile	96-hour LC_{50}	8.0	7.0	Fung and Bewick 1980
Whitefish (*Coregonus clupeaformis*) – sac fry	96-hour LC_{50}	8.0	2.0	Fung and Bewick 1980
Yellow perch (*Perca flavescens*) – sac fry	96-hour LC_{50}	8.0	<2.0	Fung and Bewick 1980
California killifish (*Fundulus parvipinnis*)	96-hour LC_{50}	8.3	1430	Bagarinao and Vetter 1993
Freshwater crayfish (*Procambarus clarkii)*	447-day NOEC (survival)	7.69–7.73	4.1	US EPA 1976
Ephemeroptera (*Hexagenia limbata*) – nymph	138-day NOEC (survival)	7.8–8.2	12.9	US EPA 1976

Species	Duration and Test Endpoint	pH During Test[b]	Value (µg/L)	Reference
Bluegill *(Lepomis macrochirus*)	126-day NOEC (reproduction)	7.6–8.0	0.4	Smith et al. 1976; US EPA 1976
Bluegill *(Lepomis macrochirus*)	97-day LOEC (reproduction)	7.6–8.0	1.0*	Smith et al. 1976; US EPA 1976
Goldfish (*Carassius auratus*)	430-day LOEC (final weight)	7.57–7.63	9.0	US EPA 1976
Freshwater tropical fish (*Mystus nemurus*)	6-week LOEC (decreased growth rate and decreased liver somatic) index)	6.9–7.5	0.5	Hoque et al. 1998
Sea urchin (*Lytechinus pictus*)	49-day LOEC (decreased wet weight)	8.0	1.12	Thompson et al. 1991
White shrimp (*Metapenaeus monoceros*)	48-hour LC_{50}	8.0–8.4	8.7	Kang and Matsuda 1994
White shrimp (*Metapenaeus monoceros*) – juvenile	48-hour LC_{50}	8.0–8.2	18.5	Kang and Matsuda 1994

[a] For freshwater tests, water hardness was within the accepted range (50 mg/L–250 mg/L as $Ca\text{-}CO_3$).
[b] Studies did not always indicate whether reported pH values represented mean values.
* Value selected as the critical toxicity value (CTV) for calculating the predicted no-effect concentration (PNEC) for the aquatic exposure scenarios in the ecological risk characterization section.

Hydrogen sulfide in sediments has the potential to harm benthic organisms, and it has been suggested that it may be responsible for some unintended toxicity in sediment bioassays (Wang and Chapman 1999). However, when released to water, hydrogen sulfide is expected to be removed rapidly by both oxidation and volatilization. Consequently, very little exposure of benthos is likely to result from anthropogenic releases to water. Sulfides that are found in sediments are typically produced *in situ* by sulfate-reducing bacteria during the decomposition of organic materials. As a result, micromolar to millimolar levels of sulfide have been measured in natural fresh and marine porewater (Wang and Chapman 1999). Because the presence of hydrogen sulfide in sediments is primarily due to natural processes, its toxicity to benthos is not evaluated in this assessment.

7.1.3 Effects on terrestrial organisms

7.1.3.1 Effects on plants

The effects of hydrogen sulfide on terrestrial plants may be beneficial or harmful at low air concentrations. Beneficial effects could in some cases be due to alleviation of a sulfur nutrient deficiency. However, under controlled experimental conditions (with adequate supplies of nutrients), it is more likely an indication of hormesis (that is, a tendency for certain potentially toxic chemicals to cause stimulatory effects associated with stress induced at low dosages) (Taylor and Selvidge 1984).

The effects of hydrogen sulfide on primary root growth in the *Arabidopsis* spp. plant were reported by Zhang et al. (2017). Hydrogen sulfide toxicity repressed primary root growth by reducing the meristematic cell division potential. High concentrations of hydrogen sulfide induced reactive oxygen species (ROS) production via the nicotinamide adenine dinucleotide phosphate hydrogen (NADPH) oxidase pathway, which directly inhibited primary root growth and activated mitogen-activated protein kinase 6 (MPK6) (intra- and extracellular signalling in eukaryotes).

Available toxicity data for terrestrial plants are reviewed in WGAQOG (2000) and Alberta Environment (2004a). These reviews reported approximately 60 individual toxicity results for over 30 horticultural, agricultural, and forest species. Although some studies described effects from exposures of short durations (a few hours or less), most involved longer-term exposures ranging from several days to up to several months.

Most of the identified studies of short duration did not report on relevant effect measures (for example, reduced growth or survival), and exposure concentrations were high (>50 000 µg/m^3). One relevant study of acceptable quality by Taylor and Selvidge (1984) examined the effects of exposure concentrations in the 208 µg/m^3 to 2788 µg/m^3 range (6.1 µmol/m^3 to 81.8 µmol/m^3) on rates of photosynthesis in bush bean (*Phaseolus vulgaris)*. Exposure occurred 5 to 7 weeks after germination in open gaseous exchange systems. Rates of photosynthesis were measured at 30-minute to 1-hour intervals for a total of 6 hours. The initial (1 and 2 hour) effects of the two lowest concentrations (208 µg/m^3 to 419 µg/m^3) were stimulatory,

with rates of photosynthesis ranging from 109% to 125% of controls. Based on this study, the lowest concentration associated with evidence of reduced photosynthesis (a reduction of approximately 10%) after exposure for 1 to 2 hours was 984 µg/m^3 (32.7 µmol/m^3). The lowest-observed-effect concentration after 6 hours of exposure was 208 µg/m^3, which caused a 15% reduction in photosynthesis relative to controls. Taylor and Selvidge (1984) reported that the relationship between photosynthesis and hydrogen sulfide dosage (defined as concentration multiplied by hours of exposure) was statistically significant, with a second-degree polynomial regression accounting for approximately 82% of the observed variation in photosynthesis rates.

The overall lowest adverse effect level in a long-term study of acceptable quality was reported by Thompson and Kats (1978). These authors exposed seven species, mostly agricultural, to continuous uniform fumigations of hydrogen sulfide in greenhouses over periods of about two to five months. Temperatures were maintained near ambient levels (for Duarte, California). At 100 ppb (140 µg/m^3), grape plants (*Vitis vinifera*) exhibited a statistically significant 30% decrease in cane dry weight relative to controls. Dry weight is considered a more reliable measure of yield than fresh weight, since the latter is partly a function of water status at the time of harvest (WGAQOG 2000). Although alfalfa (*Medicago sativa L.*) exhibited a 10% yield reduction when exposed to the same hydrogen sulfide concentration, the authors reported that this result was not statistically significant. They further noted that the 140 µg/m^3 concentration had a stimulatory effect on some other species tested. Exposure at the next highest test concentration of 300 ppb (420 µg/m^3) resulted in harmful effects in six of the seven species tested. The lowest tested concentration of 30 ppb (42 µg/m^3) frequently had a statistically significant stimulatory effect and was never associated with evidence of reduced yield.

Another longer-term study by Maas et al. (1987) reported similar effect levels. These authors exposed three agricultural species for two weeks. They reported a statistically significant 32% reduction in the fresh weight of clover (*Trifolium pratense*) and a smaller but significant increase of 11% in the fresh weight of dwarf French bean (*Phaseolus vulgaris*) at an exposure concentration of 350 µg/m^3.

The available data from long-term studies thus suggest that only stimulatory effects are likely in plants exposed to up to approximately 50 µg/m^3 hydrogen sulfide (Thompson and Kats 1978).

The lowest reported long-term adverse effect level of 140 µg/m^3 reported by Thompson and Kats (1978) will be used as a CTV to determine a PNEC for terrestrial plants exposed for longer periods (that is, weeks or months). The lowest short-term exposure effect level of 984 µg/m^3 reported by Taylor and Selvidge (1984) will be used as a CTV to determine a PNEC for plants exposed for short periods (that is, 1 to 2 hours).

7.1.3.2 Effects on wildlife

Hydrogen sulfide inhibits the mitochondrial electron transport system, which could cause cellular toxicity via reduced adenosine triphosphate (ATP) production and/or generation of oxidative stress (Jiang et al. 2016). The effects of the substance are expected to behave similarly in all vertebrate species that utilize aerobic metabolism, such as birds, mammals, certain reptiles, and amphibians (Dombkowski et al. 2005). Lusk and Kraft (2010) modelled the dose and potential response of several reptiles, mammals, and migratory birds in order to evaluate the toxicity of hydrogen sulfide to wildlife. Based on dosimetric calculations, mammals appear to be more sensitive to hydrogen sulfide than birds or reptiles.

Hydrogen sulfide concentrations of less than 2.9 mg/m^3 (2 ppm) do not appear to cause an effect on mammal species at rest, while concentrations greater than 7.2 mg/m^3 (5 ppm) pose a risk to wildlife and are likely to affect their olfactory senses, irritate their eyes and mucus membranes, or dilate their blood vessels and cause a startle or stress reaction (Lusk and Kraft 2010).

Lusk and Kraft (2010) conducted counts of migratory birds in habitat areas impacted by oil and gas production activities in Texas. Between November 2002 and August 2003, they found that avian diversity and number of species were significantly lower at disturbed sites (areas affected by oil and gas activities and elevated hydrogen sulfide concentrations, 33 ppm) in comparison with undisturbed sites (areas without oil and gas activities within 250 meters).

Appendix B contains a summary of the health effects information for mammals (including humans) that was reviewed for the human health portion of this assessment. An inhalation-based lowest-observed-effect concentration (LOEC) of 14 mg/m^3 (10 ppm) reported by Lopez et al. (1987) was among the most sensitive laboratory-based acute inhalation results. The effect observed was a significant increase in the cellularity of nasal lavage fluid after 4 hours of exposure, although levels returned to original levels at 20 hours post-exposure in male Fischer 344 rats. With regard to the effects of longer-term exposures, Dorman et al. (2000) reported that a LOEC of 14 mg/m^3 (10 ppm) was observed in adult Sprague-Dawley rats exposed for 6 hours per day, 7 days a week, for several weeks, based on decreased absolute and relative adrenal weights in males and decreased relative ovary weights in females.

The Western Interprovincial Scientific Studies Association conducted a study (WISSA 2006) to determine if chronic exposure of cattle (prenatal to 3 months postnatal) to air emissions (including hydrogen sulfide) from oil and gas industry activities influenced cattle health and reproductive behaviour in western Canada. Passive air monitors located on or near all occupied pastures and wintering areas measured hydrogen sulfide at 1100 sites from April 2001 to January 2003. An individual monthly exposure was calculated for each animal based on the air concentration at a given location and on the time spent by the animal near that location. The primary effects endpoints considered were reproductive success and development,

and the secondary effects endpoints were immune system pathology and function. The potential for effects (including reduced hatching and fledgling success) on wild European starlings (*Sturnus vulgaris*) occupying the same areas as the cattle was also evaluated (WISSA 2006). Results for the beef cattle and European starlings were negative; that is, no evidence was found of associations between the measured average monthly exposures (arithmetic mean 0.24 µg/m^3 and 95th percentile 0.74 µg/m^3) and most of the health outcomes. Increased exposure to hydrogen sulfide and sulfur dioxide did result in increased heterophil/lymphocyte ratios in starlings during one year of the study. However, it was concluded that this would likely have little effect on nestling immune competence (WISSA 2006).

Additional information on the effects of hydrogen sulfide on livestock and wildlife is summarized in WGAQOG (2000). These authors note that although ambient concentrations of hydrogen sulfide have not been shown to have adverse effects on wildlife, high concentrations (usually hundreds of mg/m^3) due to accidental releases have resulted in the deaths of wild animals and birds. In keeping with results from the study by Lopez et al. (1987), non-lethal effects on cattle exposed to concentrations of about 14 mg/m^3 (10 ppm), the result of accidental releases (blow-out of Alberta gas wells), were reported to include runny noses and eyes, coughing, and decreased feed consumption (WGAQOG 2000).

For inhalation toxicity to wild mammals, a CTV of 14 mg/m^3 based on the 4-hour LOEC in rats (Lopez et al. 1987) will be used to determine the short-term exposure PNEC, and a CTV of 14 mg/m^3 based on the rat 4-week LOEC (Dorman et al. 2000) will be used to determine a long-term exposure PNEC for terrestrial mammals and birds.

7.2 Ecological exposure assessment

Hydrogen sulfide has been measured/estimated for Canadian air, surface water, and effluent from publicly owned and industrial wastewater treatment facilities.

This section presents measured environmental concentrations of hydrogen sulfide, including available monitoring information. The focus is on measurements made at or near oil and gas facilities, pulp and paper operations, wastewater treatment systems, and intensive livestock operations.

7.2.1 Air

A summary of studies measuring levels of hydrogen sulfide in air, including ambient air and near point sources, is provided in Appendix C.

Ambient air quality objectives for hydrogen sulfide developed by Canadian provinces are based on the concentrations at which humans can begin to detect odours (British Columbia 2016). The objectives are reported for total reduced sulfur (TRS) compounds and are measured as hydrogen sulfide.

The reported value of 1 ppb (1.4 µg/m^3) is considered to be the average concentration found in urban areas away from point sources (Alberta Environment 2000a).

The US EPA (1993) has reported that concentrations of hydrogen sulfide in ambient air from natural sources are typically less than about 0.3 ppb or 0.5 µg/m^3.

7.2.1.1 Oil and gas facilities

Numerous monitoring stations in Alberta take continuous, hourly measurements of hydrogen sulfide concentrations in air, and data are available from the Clean Air Strategic Alliance (CASA) Data Warehouse website.

The CASA Data Warehouse is a publicly available database of continuously stored air pollutant concentrations and is operated by several organizations, including Alberta Environment and Environment and Climate Change Canada. Mean and 99th percentile concentrations of hydrogen sulfide were calculated from a review of the CASA data from the 35 monitoring sites near oil sands facilities between May 2007 and May 2017. The Bonnyville station reported the highest 99th percentile concentration of 15 ppb (20.9 µg/m^3) (CASA 2017). The maximum concentration reported across all stations was 113 ppb (162 µg/m^3) at the Scotford Station No. 2 on October 15, 2015 (Appendix C, Table C-2). The highest mean of all hourly samples at each station between May 2007 and May 2017 was 0.97 ppb (1.35 µg/m^3).

In the Fort McMurray and Wood Buffalo airshed region, 99th percentile concentrations of 0.4 ppb to 6.5 ppb (0.57 µg/m^3 to 9.36 µg/m^3) hydrogen sulfide from continuous monitoring were reported in 2018 (WBEA 2018). The majority of hydrogen sulfide emissions are from upgraders and tailings ponds. In 2015, hydrogen sulfide was measured at an annual average concentration of 0.3 ppb to 0.7 ppb (0.42 µg/m^3 to 0.98 µg/m^3) at 19 fixed sites in Alberta near oil sands plants (WBEA 2016). The maximum 1-hour and 24-hour average concentrations from this study were 36 ppb (50.4 µg/m^3) and 6 ppb (8.4 µg/m^3), respectively. In 2014, hydrogen sulfide was measured at an average hourly concentration of 0.2 ppb to 0.3 ppb (0.28 to 0.42 µg/m^3) in the Western Yellowhead Air Management Zone, Saskatchewan (AMEC 2014). In the same study, maximum 1-hour and 24-hour average concentrations of 13.5 ppb (18.9 µg/m^3) and 2.3 ppb (3.22 µg/m^3), respectively, were reported. Between August 2013 and August 2016, an average hourly concentration of <1 ppb (<1.4 µg/m^3) of total reduced sulfur was reported in Saint John, New Brunswick, of which up to 60% may be hydrogen sulfide (New Brunswick 2016). In the same study, 99th percentile and maximum hourly concentrations of 0.6 ppb to 1.2 ppb (up to 0.84 µg/m^3 to 1.68 µg/m^3) and up to 10.8 ppb (up to 15.12 µg/m^3), respectively, were reported, based on the assumption that up to 60% of total reduced sulfur is hydrogen sulfide.

According to Taylor (2017), maximum hourly concentrations at six monitoring sites near six rural communities associated with oil and gas development in northeastern BC (2013–2017) ranged from 3.1 ppb to 64.5 ppb (4.4 µg/m^3 to 92.9 µg/m^3) of total reduced sulfur, the prime component of which is hydrogen sulfur (2.63 µg/m^3 to 55.74 µg/m^3, assuming up to 60% of TRS is hydrogen sulfide).

The Southeast Saskatchewan Airshed Association (SESAA), a non-profit organization of public, industry, government, and non-government members, collects air quality data for the southeast Saskatchewan region. The southeast Saskatchewan airshed encompasses an area of approximately 36 800 km^2 in a region where major economic activities include natural gas and petroleum production. In 2017, the continuous air monitoring network consisted of seven air monitoring stations (SESAA 2018). Annual average concentrations for continuous monitoring of hydrogen sulfide ranged from 0.5 ppb to 1.0 ppb (0.72 µg/m^3 to 1.44 µg/m^3).

Annual average concentrations of 0.58 µg/m^3 to 0.72 µg/m^3 hydrogen sulfide were reported for two monitoring sites located in west-central Saskatchewan for 2016 (WYAMZ 2016). At these sites, data from the continuous air monitoring of hydrogen sulfide at three monitoring stations located in the southern and central region of Saskatchewan were collected by the Great Plains Air Zone in 2018 (GPAZ 2018). The annual average concentration was 0.6 ppb (0.86 µg/m^3) at the Pense station and 0.9 ppb (1.29 µg/m^3) at the Yorkton station. A maximum 1-hour concentration of 18.5 ppb (26.6 µg/m^3) and a maximum 24-hour concentration of 3.7 ppb (5.3 µg/m^3) were reported at the Yorkton station.

In 2014 and 2015, annual average and maximum 24-h and 1-hr total reduced sulfur concentrations of up to 0.8 ppb (up to 0.504 µg/m^3), 2.0 ppb, and up to 20 ppb (up to 8.4 µg/m^3), respectively, were reported in a First Nations community in southwestern Ontario, on the basis of the assumption that up to 60% of total reduced sulfur is hydrogen sulfide (OMECC 2017). In 2014, monthly average hydrogen sulfide concentrations of 0.08 to 0.86 ppb (0.11 to 1.24 µg/m^3) were reported in northeastern Alberta (FAP 2015). In the same study, maximum 1-hour and 24-hour average concentrations of 22 ppb (30.8 µg/m^3) and 3 ppb (4.2 µg/m^3), respectively, were reported.

Concentrations of hydrogen sulfide were measured before and after the introduction of a gas production facility on Sable Island, a remote marine site off Nova Scotia (Hayes 2013). Mean and maximum hydrogen sulfide levels before the introduction of the gas production facility were 0.215 ppb (0.31 µg/m^3) and 1.2 ppb (1.72 µg/m^3), respectively. In comparison, the mean and maximum levels of hydrogen sulfide after the facility became operational were 0.48 ppb (0.69 µg/m^3) and 13.7 ppb (19.7 µg/m^3), respectively. Using modelling (Positive Matrix Factorization modelling) and a Spearman’s rank order correlation, the author concluded that offshore oil and gas activities contributed to increased concentrations of H_2S on Sable Island.

Four monitoring stations are located in the Northwest Territories (Yellowknife, Inuvik, Fort Liard, and Norman Wells). In 2014, the maximum hourly hydrogen sulfide concentration was 2.0 ppb (2.88 µg/m^3), and the maximum 24-hour average was 1.8 ppb (2.6 µg/m^3). From 2010 to 2012, the maximum recorded 1-hr average ranged from 1 ppb to 2.77 ppb (1.44 µg/m^3 to 4 µg/m^3), while the maximum 24-hr average ranged from 0.2 to 2.77 ppb (0.28 µg/m^3 to 4 µg/m^3) (NWT 2010, 2012, 2014). In 2012, the vast majority of readings were less than 1.44 µg/m^3.

Hourly concentrations were reported at the Cameron Hills upstream oil and gas facility in the Northwest Territories from May 2008 to April 2009, with a maximum hourly concentration of 58 ppb (83.5 µg/m^3) hydrogen sulfide in June 2008 while average monthly concentrations ranged from 0.1 ppb (0.14 µg/m^3) to 0.7 ppb (1.0 µg/m^3) (Chepelkevitch 2009). Passive monthly concentrations of hydrogen sulfide ranged from 0.02 ppb to 19.1 ppb (0.03 µg/m^{3}27.5 µg/m^3) from March 2004 to April 2009 in the communities of Inuvik, Fort Liard, and Normal Wells. Girard (2007) reported monthly average hydrogen sulfide concentrations ranging from 0 ppb to 0.6 ppb (0.86 µg/m^3) from May 2006 to April 2007.

WGAQOG (2000) summarized some older data on hydrogen sulfide in air collected from 93 monitoring stations across Canada for the period of January 1989 to December 1998. Of the sampling sites, 14 were at oil and gas facilities and 6 were at oil sands sites. The 99th percentile hourly concentration associated with oil and gas refineries was 12 ppb (16.8 µg/m^3), while that for oil sands facilities was 7 ppb (9.8 µg/m^3).

Additional information on concentrations in air in the vicinity of oil and gas facilities is presented in Appendix C.

7.2.1.2 Publicly owned wastewater treatment systems

Wastewater treatment systems can release hydrogen sulfide to air as well as to water. In late November 2014, hydrogen sulfide was measured at an hourly concentration of 25 ppb (35 µg/m^3; statistical metric unspecified) near a wastewater treatment system in Alberta (Asquith 2016; Reiger 2016; Morin 2016).

At an air monitoring station near the Bonnybrook wastewater treatment system in Calgary, Alberta, a maximum monthly average concentration of 1.4 ppb (2 µg/m^3) and a maximum 1-hour value of 38 ppb (53 µg/m^3) were reported, based on data from January 1989 to July 2003 (Hoeksema 2004).

7.2.1.3 Pulp and paper mills

Environment Canada (2004b) reported total reduced sulfur concentrations in 1-hour air samples at 50 pulp and paper mills across Canada, representing a period from the mid-1990s to 2003. The 99th percentile and/or maximum concentrations were estimated for each monitoring site, with the highest 99th percentile 1-hour total reduced sulfur concentration reported to be 31 ppb (44.67 µg/m^3) at a mill in Ontario in 2001. The average annual concentration of 1.7 ppb (2.45 µg/m^3) estimated for an Ontario mill was also the highest average annual value reported nationally. Based on the assumption that up to 60% of total reduced sulfur can be composed of hydrogen sulfide (Environment Canada 2004b), this corresponds to hydrogen sulfide concentrations of up to 18.6 ppb (26.84 µg/m^3).

As mentioned previously, WGAQOG (2000) summarized data for hydrogen sulfide in air from 93 monitoring stations across Canada for the period of January 1989 to December 1998. Sixty-four of the sampling sites were located near pulp and paper mills. The 99th percentile hourly concentration associated with pulp and paper mills was reported as 31 ppb (43.4 µg/m^3), the highest across all of the sectors examined. The overall maximum reported hourly concentration for all sectors—503 ppb (724 µg/m^3)—was also measured near a pulp and paper mill, as was the highest monthly average concentration of 3.9 ppb (5.5 µg/m^3).

7.2.1.4 Intensive livestock operations

Intensive livestock operations are widespread across Canada. Hydrogen sulfide was measured both upwind and downwind of a beef cattle, a dairy cattle, a poultry, and a swine confined feeding operation in Alberta over a 14-month period (Alberta Government 2011). The mean, minimum, median, and maximum 1-hour average hydrogen sulfide concentrations were measured at each mobile station with respect to all wind directions in each measurement period. The median 1-hour average concentrations ranged from non-detect to 0.63 ppb (0.90 µg/m^3), and from non-detect to 0.62 ppb (0.89 µg/m^3) at mobile stations one and two, respectively. Maximum 1-hour concentrations for mobile stations one and two ranged from 0.49 ppb (0.70 µg/m^3) to 6.59 ppb (9.5 µg/m^3), and from 0.68 ppb (0.98 µg/m^3) to 22.8 ppb (32.85 µg/m^3), respectively.

The maximum 1-hour concentration of hydrogen sulfide at two swine feeding operations was 76 µg/m^3 and 26 µg/m^3 in the Lethbridge, Alberta area. Hydrogen sulfide levels monitored at all other sites ranged from 1.4 µg/m^3 to 11 µg/m^3 (Alberta Environment 2000b).

Air quality surveys were conducted 300 m downwind of an injected field site near a group of swine rearing facilities south of Girouxville, Alberta (Alberta Environment 2007). A maximum concentration of 1.41 µg/m^3 (0.001 ppm) hydrogen sulfide was reported for the fall 2006 survey.

A monitoring study on confined feeding operations (CFOs), carried out from October 2007 to September 2008 by the Peace Airshed Zone Association (PASZA 2011), reported a maximum 1-hour concentration of 21 µg/m^3 (14.9 ppb) near Girouxville. For over 90% of the study duration, hydrogen sulfide concentrations were at or below the 1.4 µg/m^3 (1 ppb) detection limit of the instrument at the station. The highest concentrations of hydrogen sulfide were observed during the winter months when conditions favour poor dispersion, particularly during temperature inversions. The authors reported that elevated hydrogen sulfide concentrations appear to occur during the early fall months (September and October) and again in the late spring months (May and June) and may be related to manure spreading operations or the emptying of the manure slurry lagoons.

If proper manure management practices are followed at intensive livestock operations, hydrogen sulfide from manure application to land will be incorporated into the soil using techniques that minimize evaporative losses.

7.2.1.5 Incidental exposure

In addition to concentrations of hydrogen sulfide reported from continuous air ambient monitoring from publicly available sources as described above, a number of incidents have been reported of high concentrations of hydrogen sulfide in air over short periods of time. Data on these incidents have been provided by provincial and local governments and agencies, mainly in Ontario. It is reasonable to expect that some inactive oil and gas wells in other provinces and/or territories also produce incidental releases of hydrogen sulfide, although such data are lacking.

Notably, data are available indicating incidents of high hydrogen sulfide release associated with inactive oil and gas wells. The measured data from the incidental release of hydrogen sulfide from these wells have been shown to be sporadic and irregular, and may persist for several hours.

Incidents of high hydrogen sulfide concentrations were measured in air at a number of rural and mixed-use properties in southern Ontario. At one rural property (in the vicinity of the City of Hamilton, and Haldimand and Norfolk Counties), up to 6 ppm (8646.9 µg/m^3) of hydrogen sulfide was measured in 2017. The property contains a number of inactive oil and gas wells (personal communication, email from the Ministry of Environment and Climate Change, Government of Ontario, to the Existing Substances Risk Assessment Bureau, Health Canada, dated April 2018; unreferenced).

At another location in the area of Haldimand and Norfolk Counties, data were gathered using automated sensors that recorded hydrogen sulfide concentrations in air at 1-minute intervals from early 2018 to early 2019. Over a 4-day period during the summer months of 2018, median hydrogen sulfide levels were recorded at 6 ppm (8646.9 µg/m^3), and peak levels of hydrogen sulfide were up to 180 ppm (259 407 µg/m^3) (personal communication, emails from the Haldimand-Norfolk Health and Social Services, to the Existing Substances Risk Assessment Bureau, Health Canada, dated February 2019; unreferenced).

Additional data were collected from inspection reports by the Ontario Ministry of Natural Resources and Forestry (MNRF) from 2010 onwards in southern Ontario. Of 65 point-in-time measurements of hydrogen sulfide, 59 reports indicated hydrogen sulfide levels that were greater than or equal to 2 ppm (2882 µg/m^3). Of these 59 reports, 24 reported levels between 10 ppm and 100 ppm (14411 µg/m^3 and 144 115 µg/m^3), and 16 reported levels of 100 ppm or greater. These measurements were taken with equipment used for personal safety that record point-in-time gas concentrations in the breathing zone of workers conducting field activities (personal communication, email from the MNRF, Government of Ontario, to the Existing Substances Risk Assessment Bureau, Health Canada, dated June 6, 2018; unreferenced).

According to a media report from Oxbow, Saskatchewan (Cribb 2017), levels greater than 100 ppm (144 115 µg/m^3) of hydrogen sulfide were reported on a residential property in the vicinity of oil field operations.

Further information concerning incidents of elevated hydrogen sulfide concentrations is presented in section 8.1.2 and Appendix D.

7.2.2 Water

Concentrations of dissolved hydrogen sulfide in water and wastewater are estimated indirectly from measured dissolved sulfide concentrations. As indicated in Table 3-1, the proportion of un-ionized H_2S to dissolved bisulfide ion (HS^-) varies mainly as a function of water pH. When estimating concentrations of hydrogen sulfide using water pH data and measured dissolved sulfide levels, it is typically assumed that most of the dissolved sulfides detected are present as free bisulfide (HS^-) ions or as un-ionized hydrogen sulfide.

Standard methods of quantifying dissolved sulfides typically measure “acid-labile” species (Bowles et al. 2003). These are the sulfides (for example, HS^-) liberated as gaseous H_2S when acid is added to a water sample. However, it has only been recently recognized that oxic surface water typically contains significant amounts of dissolved and colloidal metal sulfides (for example, $FeS_{(aq)}$, $ZnS_{(aq)}$), which can also be liberated by such methods (Adams and Kramer 1999; Bowles et al. 2003; Sukola et al. 2005). Because of the high affinity of dissolved metals for sulfide and the instability of free sulfide in oxic water, it is theoretically probable that the vast majority of the acid-labile sulfide detected in oxic surface water and wastewater is actually in the form of dissolved metal (particularly iron) sulfides, as described in Adams and Kramer (1999) and Sukola et al. (2005).

Only one study was identified that measured concentrations of different dissolved sulfide species in oxic fresh water and wastewater. Rozan et al. (2000) measured total dissolved sulfide concentrations as well as concentrations of $FeS_{(aq)}$, $FeSH^+_{(aq)}$, $CuS_{(aq)}$, $ZnS_{(aq)}$, and polysulfides (S_x^{2-}) in water samples from seven rivers and in wastewater samples from two wastewater treatment systems in northeastern United States. They noted that HS^- was one of the species that could contribute to their measured total dissolved sulfide results. Assuming, as previously noted, that in addition to free H_2S/HS^- it is mostly dissolved iron and zinc sulfides that contribute to measured acid-labile sulfide concentrations, the results of Rozan et al. (2000) suggest that no more than about 15% of dissolved sulfide concentrations determined by standard methods could be present as free H_2S/HS^- (Doyle 2013). Considering the likely uncertainties in the concentrations reported by Rozan et al. (2000), this percentage should be considered no more than a rough upper-bound estimate (Tessier 2013). The actual percentage of dissolved sulfide concentrations is expected to be much lower because several different sulfide species in addition to H_2S/HS^- (for example, $AgS_{(aq)}$, $CdS_{(aq)}$, $HgS_{(aq)}$, $PbS_{(aq)}$, and $S_{(aq)}^0$) could have contributed to the 15% estimated, and more importantly,

because free H_2S/HS^- is inherently unstable in oxic water, with losses occurring by both reaction and volatilization (Bowles et al. 2003; Sukola et al. 2005).

The potential to find free bisulfide ions in oxic water is greatly reduced when concentrations of dissolved iron (and other metals) are higher than those of dissolved sulfide (Luther 2013), expressed on a molar basis. In this situation, depending on the relative concentrations of and affinities for other ligands, the metals will tend to react with the available sulfide to form relatively stable dissolved metal-sulfide complexes.

In fact, it is common for dissolved metals (especially iron) to be more abundant than sulfide in oxic surface water and wastewater. For example, in a study of several lakes in Quebec by Sukola et al. (2005), molar concentrations of dissolved iron were reported to be more than two orders of magnitude above molar acid-labile sulfide levels. Similarly, Rozan et al. (2000) reported high concentrations of dissolved iron compared with sulfide in samples of water and wastewater from the northeastern United States. In addition, limited spot-checking of unpublished data on dissolved sulfide and iron levels in the Athabasca and other rivers of northern Alberta (Alberta Environment 2013) indicates that molar dissolved iron concentrations are almost always higher than those of acid-labile dissolved sulfide, typically by two or more orders of magnitude.

It has therefore been assumed in this assessment that at least 85% of dissolved sulfide concentrations measured using standard analytical methods is in the form of iron (and zinc) sulfides, and that no more than about 15% is in the form of free H_2S/HS^-. However, as explained above, the actual percentage present in the form of H_2S/HS^- is in most cases expected to be much lower. In line with this expectation, Luther et al. (2003) reported finding significant amounts of $FeS_{(aq)}$ using voltametric scans but only traces of H_2S in water at the oxic-anoxic interface of a stratified man-made lake in Pennsylvania, with an excess of dissolved iron relative to sulfide. Similarly, Rozan and Benoit (1999) reported finding no indication of free HS^- but significant amounts of dissolved copper-sulfide complexes in oxic, relatively metal-rich water samples taken from four rivers in southern New England. Consequently, the concentrations presented in this section of the report, determined by assuming that no more than 15% of measured dissolved sulfide is in the form of free H_2S/HS^-, are referred to as “upper-bound” values.

It should be mentioned that unless precautions are taken (for example, addition of zinc acetate preservative to sampled water), it is possible that some H_2S/HS^- will be lost from water samples by either oxidation or volatilization prior to analysis (Holm et al. 2000). In addition, there is evidence that some dissolved metal sulfides are lost from water by adsorption onto the walls of sample containers and when samples are passed through filters to remove suspended solids (Bowles et al. 2003). This could lead to an underestimation of concentrations. However, results of laboratory tests by Bowles et al. (2003) suggest that such losses may be significantly mitigated by the presence of the organic matter commonly found in natural water and wastewater.

7.2.2.1 Remote locations

Two published studies were identified that reported concentrations of dissolved sulfides in samples of oxic Canadian fresh water obtained in areas where there is little potential for contamination. Nanogram per litre concentrations of dissolved sulfide (maximum of about 100 ng/L) were reported in three Quebec lakes and three rural Ontario water bodies by Sukola et al. (2005) and Bowles et al. (2003), respectively. Using these reported dissolved sulfide values and water pH data (pH ranged from 5.6 to 7.7), and assuming as explained above that at least 85% of measured sulfide is complexed with iron, upper-bound concentrations of un-ionized hydrogen sulfide in these relatively pristine waters are estimated to range from 0.001 µg/L to 0.02 µg/L. Although relevant data are limited, these results suggest that concentrations of un-ionized hydrogen sulfide in uncontaminated oxic fresh water in Canada are unlikely to ever exceed about 0.1 µg/L.

7.2.2.2 Oil and gas facilities and coal mines

Alberta Environment (2013) has collected data on dissolved sulfide concentrations in over 3000 samples of surface water in the province dating back to the late 1970s. Unfortunately, analytical detection limits for samples obtained prior to about 1990, representing perhaps half of the overall data set, were too high to provide meaningful results. Hydrogen sulfide concentrations in water samples collected more recently (throughout the 1990s and 2000s) were calculated on the basis of available dissolved sulfide data and estimated water pH (typically 8.0), assuming as explained above that at least 85% of measured sulfide is complexed with iron. In fact, the percentage complexed with iron is likely to be much more than 85%, since results of spot-checks indicate that molar concentrations of dissolved iron are almost always higher than those of acid-labile dissolved sulfide, typically by two or more orders of magnitude, in the Athabasca and other rivers of northern Alberta (Alberta Environment 2013).

Upper-bound concentrations of un-ionized hydrogen sulfide estimated for northern Alberta rivers were generally less than 0.1 µg/L. There were, however, a few exceptions. Hydrogen sulfide concentrations of up to 320 µg/L were determined for samples of outflow water collected in 2008 from the bioreactor at an Alberta coal-fired plant. Actual concentrations were likely somewhat lower than this, since in this case sulfide was measured as a “total” concentration (including particulates) as opposed to a dissolved concentration. Unfortunately, no monitoring data were available for surface water in the vicinity of this site. High hydrogen sulfide concentrations (up to 100 µg/L) were also estimated for spring water collected in the early 1990s at an inactive Alberta oil well. However, no information is available on concentrations in nearby surface water. Somewhat elevated hydrogen sulfide concentrations (up to 0.4 µg/L) were also estimated for water samples collected over a four-year period (2008 to 2011) from the Athabasca River downstream from an oil sands operation.

Investigations into the natural and anthropogenic sources of hydrogen sulfide in groundwater in southwestern Ontario were carried out by Smal (2016) and Skuce (2014), who suggested that measured concentrations of hydrogen sulfide originated from nearby inactive gas wells. Some of these gas wells are known to be artesian on the Niagara Peninsula (MNRF 2016) and may add methane to shallow aquifers containing sulfate, resulting in sulfate reduction generating high groundwater concentrations of hydrogen sulfide (for example, <0.01 mg/L to 41.25 mg/L), with a median concentration of 5.25 mg/L (Smal 2016). Abandoned oil and gas wells provide conduits for methane and bacteria, which can then metabolize the methane, generating by-products such as hydrogen sulfide (Skuce et al. 2015). Dusseault and Jackson (2019) reported on one abandoned borehole, which had a very high flowrate (greater than 10 L/minute) and may emit hydrogen sulfide gas at greater than 100 ppm.

7.2.2.3 Pulp and paper mills

Results from the pulp and paper industry’s National Council for Air and Stream Improvement (NCASI 2012) study of 25 pulp and paper mills—located mostly in the United States but with some in Canada—indicated total dissolved sulfide levels in samples of biologically treated final effluents (the year of sample collection was not specified) ranging from non-detect (<30 µg/L) to 290 µg/L (0.29 mg/L). The average concentration was 100 µg/L and the median concentration was 70 µg/L. The study also provides estimates of hydrogen sulfide concentrations in receiving waters near the discharge points for the 25 mills. These values are based on a dilution factor that encompasses 80% of mills and takes into account low flow volumes in receiving waters. The estimated hydrogen sulfide values in receiving waters ranged from non-detect to 14 µg/L (0.014 mg/L), with an average of 5 µg/L (0.005 mg/L) and a median of 3.5 µg/L (0.0035 mg/L). However, these estimated concentrations do not account for the likely contribution of iron sulfides to their measured dissolved sulfide values. Assuming, as explained above, that the level of metal sulfide complexing is at least 85%, the upper-bound average, median, and maximum concentrations in receiving waters would be 0.75 µg/L, 0.53 µg/L, and 2.1 µg/L, respectively. In fact, as explained previously, the percentage complexed with iron may be much greater than 85%, especially since significant quantities of metals (particularly iron and manganese) are commonly found in pulp and paper wastewater (for example, Palumbo et al. 2010).

The Meadow Lake mill, located approximately 300 km north of Saskatoon, reported a smelt composition of 6% sodium bisulfide. Through a process known as the green liquor splitter system, 98% sodium bisulfide was removed (Jemaa et al. 2009), thereby reducing the amount of “smelt” containing sodium bisulfide being sent to landfills.

7.2.2.4 Publicly owned wastewater treatment systems

According to 2019 volume data reported under the *Wastewater Systems Effluent Regulations* (Canada 2012b), 28% of total effluent volume was treated to a primary level of treatment or less, while 72% of total effluent volume was treated to a secondary level of treatment or greater (ECCC 2019).

Results from a preliminary study of two publicly owned wastewater treatment systems in Canada in November 2012 and winter/spring 2013 indicated that hydrogen sulfide was not present at a detectable concentration (detection limit of 2 µg/L) (Environment Canada 2015). The wastewater system included a large, urban secondary activated sludge process and a facultative lagoon with a retention time of approximately four months. Raw influent, primary effluent, and final effluent were collected from one system, while raw influent and final effluent were collected from the second system. Hydrogen sulfide (as S^{2-}) was detected in all raw influent and primary effluent samples from both wastewater systems (n=6, and n=3 respectively) but was not present at a detectable concentration in any effluent samples (n=6). As a result, any wastewater treatment system that is “secondary or equivalent” (that is, achieving reductions of biological oxygen demand [BOD] and total suspended solids [TSS] as specified in the *Wastewater Systems Effluent Regulations* [Canada 2012b]), will also likely remove hydrogen sulfide to non-detectable levels.

A monitoring program in Quebec identified relatively high concentrations of dissolved sulfides in the effluents from a wastewater treatment system with primary treatment and non-aerated lagoon systems (MEQ 2001a,b). Samples were collected from 1997 to 1999 at 15 wastewater treatments systems across the province. The highest mean values, that is, 110 µg/L and 140 µg/L, were recorded in the summer at two wastewater treatment systems, both of which discharge to the St. Lawrence River. A mean concentration of 120 µg/L dissolved sulfide was also recorded in a lagoon sample at Martinville (located southeast of Sherbrooke) in the winter. Assuming a water pH of approximately 7.5 (a typical value for St. Lawrence River water; Ramesh 1989) and assuming, as explained above, that at least 85% of the measured dissolved sulfides are complexed with iron, the upper-bound H_2S concentrations in these effluents are estimated to be in the 4.0 µg/L to 5.0 µg/L range. In fact, the percentage complexed with iron is likely to be much more than 85% since relatively high concentrations of total extractable iron were reported in system effluents, that is, from about 200 µg/L to 1700 µg/L, depending on whether or not wastewater had been treated with ferric chloride (MEQ 2001a,b). Allowing for 10-fold dilution after release, the resulting upper-bound concentrations in receiving surface waters would be 0.4 µg/L to 0.5 µg/L.

The program also included toxicity testing of the effluents. Although it is not possible to establish unambiguous relationships between the presence of a contaminant in an effluent and the observed toxicity, the authors of the report (MEQ 2001a,b) did note that hydrogen sulfide was one of the substances that may have been responsible for some of the adverse effects observed.

In an unpublished 2003 study of water quality in the St. Lawrence River, Environment Canada researchers at the Centre St. Laurent in Quebec measured a dissolved sulfide concentration of 20 µg/L at 0.5, 1.0, and 2.5 km downstream of the outfall of a wastewater treatment system and a concentration of 10 µg/L at 7 km downstream of the outfall (Environment Canada 2004c). Assuming a pH of 7.5 (Ramesh 1989) and assuming (as previously explained) that at least 85% of the measured dissolved sulfides are complexed with dissolved iron, which is more abundant than sulfide in these waters

(Gagnon and Turcotte 2007), the upper-bound hydrogen sulfide concentrations in these waters are estimated to be 0.75 µg/L and 0.40 µg/L, respectively.

Adams and Kramer (1999) measured dissolved sulfides in effluents from wastewater treatment systems in Dundas and Burlington, Ontario, from 1997 to 1998. Both plants used an activated sludge treatment process with the addition of ferric chloride to enhance floc formation and settling in the clarifier tanks. The authors reported finding 7.1 µg/L (223 nM) in the effluent from the Dundas plant and 9.0 µg/L (280 nM) in the effluent from the Burlington plant. Samples of surface water were also taken downstream of the Dundas plant in the Desjardin Canal. Measured concentrations ranged from 6.5 µg/L (202 nM) near the plant outfall to 5.9 µg/L (184 nM) 500 metres downstream from the outfall. Assuming a pH of 7.4 (Adams and Kramer 1999) and assuming that (as previously explained) at least 85% of the measured dissolved sulfides are complexed with iron, the upper-bound hydrogen sulfide concentrations in these surface waters are estimated to be 0.27 µg/L and 0.25 µg/L, respectively.

7.3 Characterization of ecological risk

The approach taken in this ecological assessment was to examine assessment information and develop proposed conclusions using a weight-of-evidence approach and precaution. Evidence was gathered to determine the potential for the three substances in this assessment 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. Secondary or indirect lines of evidence are considered when available, including regulatory decisions and classification of hazard or fate characteristics made by other regulatory agencies.

The information collected indicates that large quantities of hydrogen sulfide are released from natural sources, mainly to air. However, release from anthropogenic sources may also be significant. Anthropogenic sources of particular importance in Canada are associated with natural gas and oil production, pulp and paper manufacturing, publicly owned wastewater treatment systems, and intensive livestock operations.

In the environment, hydrogen sulfide is found mainly in the air compartment, where it can persist for relatively long periods (it has a degradation half-life of several weeks) during cold Canadian winters. In the summer, however, it is degraded rapidly in air (half-life of <1 day) by reaction with hydroxyl radicals. It is also lost rapidly (half-lives of hours or less) from oxic water by both volatilization and oxidation reactions. However, under anoxic conditions in water, sediment, or soil, hydrogen sulfide has the potential to persist for relatively long periods of time.

As an inorganic gas, hydrogen sulfide is not expected to bioaccumulate. Experimental aquatic toxicity information suggests that hydrogen sulfide acts primarily as an acute toxicant and that it has the potential to cause harm to aquatic organisms at low concentrations, that is, within the low µg/L range in fresh water. Studies have shown that airborne exposure to hydrogen sulfide acts as a phytotoxin in some plants and may adversely affect wildlife. Thus, there is a potential concern for the environment associated with the incidental release of high levels of hydrogen sulfide from inactive oil and gas wells. Measured data from a number of incidental releases of hydrogen sulfide around inactive oil and gas wells in southern Ontario have shown that wells can release hydrogen sulfide levels greater than 100 ppm.

7.3.1 Risk quotient analysis

Risk quotient analyses were performed by comparing the various estimates of exposure (predicted environmental concentrations, PECs) with ecotoxicity information (predicted no-effect concentrations, PNECs) to determine whether there is potential for ecological harm in Canada. Risk quotients (RQs) were calculated by dividing the PEC by the PNEC for relevant environmental compartments and associated exposure scenarios. A risk quotient analysis that integrates known or potential exposures with known or potential adverse ecological effects was performed for five different scenarios. For these scenarios, conservative and representative PECs were selected from the Canadian monitoring data presented in the measured environmental concentrations section (see section 7.2.1 to 7.2.2). PNECs were determined by dividing a CTV (see section 7.1) by an assessment factor. PEC, CTV, and PNEC values used in this assessment are summarized in Table 7-2. Aquatic PECs are shown with a “less than” symbol (<) because, as explained previously, the percentage of dissolved sulfide present as free H_2S/HS^- in oxic water is expected to generally be much less than the 15% value assumed when the concentrations were calculated.

Based on continuous air monitoring data for hydrogen sulfide, a representative PEC of 20.9 µg/m^3, which corresponds to the highest 99th percentile concentration from all stations reported over the sampling period near oil sands in Alberta from May 2007 to May 2017, was selected as an estimate of short-term regional-scale atmospheric exposure near anthropogenic sources (CASA 2017). To derive short-term PNECs, CTVs for both mammals and plants were divided by an assessment factor (AF). AFs account for various extrapolations and sources of uncertainty. An endpoint standardization factor (F_{ES}) is considered for extrapolation from lethal effects (that is, mortality) to sublethal effects (for example, growth, reproduction), and from median effect levels (for example, EC_{50}) to low effect levels (for example, EC_{10}). The AF also accounts for the number of species and organism categories that are represented in the toxicity data set (species variation factor, F_{SV}) and whether the substance has a mode of action that is more toxic than baseline narcosis (mode of action factor, F_{MOA}). The final AF is derived by multiplying the F_{ES}, F_{SV}, and the F_{MOA}.

For short-term air exposure of mammals, the CTV selected was based on the rat toxicity value (4-hour inhalation-based LOEC; increased cellularity of nasal lavage fluid) of 14 mg/m^3 (14 000 µg/m^3) from Lopez et al. (1987). Since the CTV is already based on a low-level sublethal effect, the F_{ES} is equal to 1, as no further extrapolation is needed. The mode of action for hydrogen sulfide is reactive; therefore, the F_{MOA} is 2 (section 7.1.1). Since the data set for inhalation studies for hydrogen sulfide is large and comprehensive and includes three species of mammals (rat, mouse, rabbit), a F_{SV} of 1 is selected to account for variation in species sensitivities. In view of the relatively mild and transient nature of the reported adverse effect, an overall AF of 2 was used to derive the PNEC for mammals. Application of the AF to the CTV resulted in a PNEC of 7000 $\mu g/m^3$. Thus, the risk quotient (RQ = PEC/PNEC) for short-term air exposure for mammals is 0.003, based on ambient continuous monitoring data.

For short-term air exposure of plants, the CTV selected was a toxicity value of 984 $\mu g/m^3$ for bush bean (1- to 2-hour exposure causing approximately 10% reduced photosynthesis) reported by Taylor and Selvidge (1984). Given that the value is already based on low-level sublethal effects, no further extrapolation is needed and an F_{ES} of 1 will be used. Because the data set for plant studies for hydrogen sulfide is large and includes >11 species, a F_{SV} of 1 is selected to account for variation in species sensitivities. As noted above, since the mode of action for hydrogen sulfide is reactive, the F_{MOA} is 2. Therefore, the overall AF of 2 (1 × 1 × 2) is applied to the CTV of 984 $\mu g/m^3$ for terrestrial plants, resulting in a PNEC of 492 $\mu g/m^3$. The risk quotient (RQ = PEC/PNEC) for short-term air exposure of plants is 0.04, based on ambient continuous monitoring data.

For the long-term air exposure scenario that is based on continuous air monitoring data, a PEC of 27 $\mu g/m^3$ was selected, corresponding to the highest average 1-month atmospheric concentration reported in air near an anthropogenic source (an oil and gas facility; Chepelkevitch 2009). A monthly average hydrogen sulfide concentration in air is considered to be comparable to experimental exposure periods in plant toxicity studies (that is, in the range of 14 to 246 days). For long-term air exposure to mammals, the CTV selected was a LOEC of 14 mg/m^3 for decreased adrenal and ovary weights in rats exposed daily over several weeks (Dorman et al. 2000). Given that the CTV is a long-term study with a low-level subchronic endpoint, the F_{ES} is equal to 1. Since the mode of action for hydrogen sulfide is reactive (section 7.1.1), the F_{MOA} is 2. The terrestrial toxicity dataset for hydrogen sulfide includes three species covering one category; therefore, a F_{SV} of 1 was used. The overall AF of 2 (1 × 1 × 2) was applied to the CTV for mammals, resulting in a PNEC of 7000 $\mu g/m^3$. The PNEC for plants was derived from a CTV based on the chronic toxicity value (LOAEL; growth) of 140 $\mu g/m^3$ for grape vines (Thompson and Kats 1978). Since the CTV is based on a long-term sublethal study, an F_{ES} of 1 will be used. The reactive mode of action results in a F_{MOA} of 2. Since the plant toxicity data set is large and includes >11 species, a F_{SV} of one is selected to account for variation in species sensitivities. The overall AF of 2 (1 × 1 × 2) is applied to the plant CTV of 140 $\mu g/m^3$, resulting in a PNEC of 70 $\mu g/m^3$. The long-term PNECs are 70 $\mu g/m^3$ for plants and 7000 $\mu g/m^3$ for mammals. The corresponding risk quotients are 0.38 and 0.004, respectively, based on ambient continuous monitoring data.

As noted in section 7.2.1.5 and section 8.1.2, there have been a number of reports of hydrogen sulfide concentrations in air reaching up to and exceeding 100 ppm (144 115 $\mu g/m^3$) due to incidental releases from inactive oil and gas wells. Based on information from southern Ontario, the value of >144 115 $\mu g/m^3$ was selected as the PEC for incidental releases from inactive oil wells. These incidental releases contrast with other short-term exposures presented in this report (that is, those based on continuous monitoring or reflecting ambient/regional exposures) since incidental releases are typically considered unpredictable with respect to location or concentration and are often variable in magnitude and duration, reflecting the transience of hydrogen sulfide in air due to local climatic conditions (for example, wind, precipitation). Since the PEC for incidental release events reflects point-in-time measurements without any association with exact durations, and the methodologies for detection are not always known, corresponding risk quotients have not been calculated for mammals and plants. However, a general comparison indicates that the PEC is several times greater than the PNEC. Thus, it is reasonable to expect that harmful effects are anticipated for terrestrial wildlife and plants exposed to certain incidental releases from inactive oil and gas wells of sufficient duration that result in a sufficiently high concentration of hydrogen sulfide in air.

No distinction was made between short-term and long-term exposure when characterizing PECs or PNECs for surface water, since available information suggests that hydrogen sulfide generally acts as an acute aquatic toxicant regardless of exposure durations, and both acute and chronic exposures have resulted in adverse effects (Weston Solutions Inc. 2006; Smith et al. 1976).

Three aquatic scenarios were evaluated representing potential exposures downstream of pulp and paper mills, wastewater treatment plants, and oil sands facilities. PECs of <0.53 µg/L and <2.1 µg/L were used for pulp and paper facilities, representing estimated median and maximum concentrations of hydrogen sulfide in the receiving waters of 25 pulp and paper facilities located in the United States and Canada (NCASI 2012). A second PEC of <0.75 µg/L hydrogen sulfide was chosen on the basis of concentrations estimated downstream of a wastewater treatment plant in Quebec, representing potential exposures in surface waters receiving discharges from plants that use only primary wastewater treatment methods (Environment Canada 2004b). A third PEC of <0.40 µg/L was chosen to represent potential concentrations downstream of an oil sands facility. This PEC was the highest estimated concentration in six samples collected over a four-year period (2008 to 2011). In order to derive a PNEC, a CTV of 1 µg/L was selected on the basis of evidence of harmful chronic effects to aquatic species, as described above in the ecological effects assessment section (see section 7.1). This CTV was based on the 97-day LOEC (reproduction) of 1 µg/L for bluegill (*Lepomis macrochirus*) (Smith et al. 1976). Given that the aquatic data reports long-term, sub-lethal, low and no-effect values, an F_{ES} of 1 is used. The mode of action of hydrogen sulfide is reactive, resulting in an F_{MOA} of 2. Since the aquatic toxicity data set for hydrogen sulfide encompasses greater than seven species and three categories, a F_{SV} of one is applied. The overall AF of 2 (1 × 1 × 2) is thus applied to the CTV, resulting in a PNEC of 0.5 µg/L. The conservative risk quotients range from less than 0.8 to less than 4.2. Although the maximum risk quotients for aquatic organisms are slightly above 1.0, the actual percentages of sulfide that are in the form of free H_2S/HS^- are expected to be less than the value of 15% that was assumed when calculating aquatic PECs. Thus, it is considered unlikely that risk quotients based on more realistic estimates of H_2S/HS^- percentages would indicate a likelihood of harm downstream of the examined pulp and paper mills, wastewater treatment plants, and oil facilities.

Table 7-2. Risk quotients for hydrogen sulfide

Scenario	Organism	CTV	AF	PNEC	PEC	RQ (PEC/PNEC)
Short-term exposure in air - near an oil sands plant, based on continuous ambient air monitoring	Mammals	14 000 µg/m^3	2	7000 µg/m^3	20.9 µg/m^3	0.003
Short-term exposure in air - near an oil sands plant, based on continuous ambient air monitoring	Plants	984 µg/m^3	2	492 µg/m^3	20.9 µg/m^3	0.04
Long-term exposure in air - near an oil and gas facility, based on continuous ambient air monitoring	Mammals	14 000 µg/m^3	2	7000 µg/m^3	27 µg/m^3	0.004
Long-term exposure in air - near an oil and gas facility, based on continuous ambient air monitoring	Plants	140 µg/m^3	2	70 µg/m^3	27 µg/m^3	0.38
Incidental short-term exposure in air near inactive oil and gas wells	Mammals	14 000 µg/m^3	2	7000 µg/m^3	>144 115 µg/m^3	NA**
Incidental short-term exposure in air near inactive oil and gas wells	Plants	984 µg/m^3	2	492 µg/m^3	>144 115 µg/m^3	NA**
Exposure to un-ionized hydrogen sulfide	Freshwater fish and	1.0 µg/L	2	0.5 µg/L	median <0.53 µg/L*	median <1.06

in surface water downstream from pulp and paper mills	aquatic invertebrates				maximum <2.1 µg/L*	maximum <4.2
Exposure in surface water downstream from a wastewater treatment system	Freshwater fish and aquatic invertebrates	1.0 µg/L	2	0.5 µg/L	<0.75 µg/L*	<1.5
Exposure in surface water downstream from an oil sands facility	Freshwater fish and aquatic invertebrates	1.0 µg/L	2	0.5 µg/L	<0.40 µg/L*	<0.8

Abbreviations: AF, assessment factor; CTV, critical toxicity value; PEC, predicted environmental concentration; PNEC, predicted no-effect concentration; RQ, risk quotient

* A “less than” symbol (<) is used because the percentage of dissolved sulfide present as free H_2S/HS^- is expected to generally be much less than the 15% value assumed when calculating PECs for water.

** NA: Not applicable. Since the PEC for incidental release events reflects point-in-time measurements without any association with exact durations, and the methodologies for detection are not always known, corresponding risk quotients have not been calculated for mammals and plants.

7.3.2 Consideration of the lines of evidence

To characterize the ecological risk of hydrogen sulfide, sodium bisulfide, and sodium sulfide, 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 7.3, 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 of the line of evidence 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 3-3. Weighted lines of key evidence considered in order to determine the potential for hydrogen sulfide to cause harm in the Canadian environment

Line of evidence	Level of confidence[a]	Relevance in assessment[b]	Weight assigned[c]
Physical and chemical properties	high	moderate	moderate
Persistence in the environment (air, water)	moderate	moderate	moderate
PNECs for aquatic organisms	moderate	moderate	moderate
PNECs terrestrial organisms	moderate	high	moderate-high
Concentrations in wastewater effluents and surface water	low	moderate	low-moderate
Ambient monitoring air concentrations	high	low	moderate
Incidental air concentrations	moderate	high	moderate-high
RQs for aquatic organisms	low	high	moderate
RQs for terrestrial organisms	moderate	high	moderate-high

Abbreviations: PNEC, predicted no-effect concentration; RQ, risk quotient

[a] Level of confidence is determined according to data quality, data variability, and data gaps (that is, are the data 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 overall combined weights for level of confidence and relevance in the assessment.

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

There is high confidence in the physical and chemical properties of hydrogen sulfide and the two substances that have the potential to form hydrogen sulfide, sodium bisulfide, and sodium sulfide. However, the exact formation quantity of hydrogen sulfide generated from the two substances is unknown and subject to local conditions.

There is moderate confidence in the aquatic PNEC since it was based on a large data set of experimental studies showing that hydrogen sulfide is capable of exerting both acute and chronic effects on a number of aquatic organisms at low concentrations. However, there is significant uncertainty associated with estimated concentrations of hydrogen sulfide in water. After incorporating appropriate application factors, an aquatic PNEC of 0.5 µg/L was derived, which is considered very protective since it is only slightly higher than the upper range of potential natural background concentrations in water (0.1 µg/L).

There is moderate confidence in the terrestrial PNECs since data sets for both plants and wildlife with respect to air-exposure toxicity are limited. In the case of wildlife, PNECs were generated using rodent studies as a surrogate for mammalian wildlife effects. However, these PNECs are highly relevant for characterizing risk from hydrogen sulfide concentrations in air; hence, they have been ascribed an overall moderate-high weight in the assessment.

Hydrogen sulfide concentrations in surface and wastewaters are highly responsive to pH, temperature, and the presence of dissolved metals. Thus, there may be a tendency to overestimate the actual hydrogen sulfide concentrations in water and wastewater. As noted in the assessment, due to the abundance of dissolved metals in natural waters and effluents, at least 85% of dissolved sulfide concentrations are in the form of iron and zinc sulfides, and no more than 15% are in the form of hydrogen sulfide or hydrogen bisulfide anion. Even with consideration given to the formation of metal-sulfide complexes, levels of hydrogen sulfide in water are likely lower than estimated; thus, there is moderate confidence that those depicted in the assessment report are conservative enough that risk is not under-predicted.

The network of hydrogen sulfide monitoring stations has generated a large data set of ambient concentrations from several stations in Canada, and thus, there is a high confidence in the accuracy of these data. However, their relevance is limited to some extent because surveillance of incidental releases indicates that these ambient concentrations have not always captured high hydrogen sulfide concentrations in air from incidental events. Overall, ambient air concentrations are ascribed a moderate weight in the assessment. The level of confidence concerning incidental air concentrations is also moderate given the inherently unpredictable and variable nature of release data from inactive oil and gas wells and the limitations of concentrations data methodology (for example, some information was not reported, including analytical methods, detection limits, and exact location and duration of elevated hydrogen sulfide concentrations in air). The data concerning incidental releases are, however, highly relevant. There have been several accounts of extremely high hydrogen sulfide concentrations in air originating from inactive oil and gas wells and exceeding 100 ppm, which is several times higher than the short-term PNEC. These levels are well above the range of potential effects on plants and mammals from short duration exposures. It is estimated that there are 261 000 inactive wells in the western provinces (British Columbia, Alberta, Saskatchewan) and over 11 000 inactive wells recorded in Ontario, and it is reasonable to expect that some may also be associated with incidental hydrogen sulfide releases although there are a lack of data to confirm this possibility. Thus, the available data concerning incidental releases may not adequately characterize the potential frequency and magnitude of these exposures across Canada. These factors also combine to ascribe a moderate-high weight to the concern associated with these incidental releases. This information indicates that hydrogen sulfide from incidental releases from inactive oil and gas wells has the potential to cause ecological harm in Canada. Sodium bisulfide and sodium sulfide are not expected to be released to air because of their low vapour pressure. Uses of sodium bisulfide and sodium sulfide are not associated with hydrogen sulfide exposures of concern and therefore have low potential to cause ecological harm in Canada.

7.3.4 Sensitivity of conclusion to key uncertainties

One source of uncertainty relates to the measurement of hydrogen sulfide and involves the method for determining concentrations of un-ionized hydrogen sulfide in freshwater. Concentrations of hydrogen sulfide are normally estimated on the basis of measured concentrations of dissolved sulfide, information on pH, and sometimes temperature of the receiving waters. In so doing, it is normally assumed that most of the measured dissolved sulfide is in the form of the free bisulfide (HS^-) ion or un-ionized hydrogen sulfide. However, a study of sulfide speciation in oxic surface water suggests that at least 85% of dissolved sulfide concentrations measured using standard methods is present as dissolved iron sulfides—principally FeS and $FeSH^+$—and that no more than 15% could be in the form of free H_2S/HS^-. In this assessment, reported dissolved sulfide levels were consequently multiplied by a factor of 0.15 when concentrations of un-ionized hydrogen sulfide were estimated. The 15% value for un-ionized hydrogen sulfide should, however, be considered only a rough upper-bound estimate. In fact, given the inherent instability of hydrogen sulfide in oxic water and since available data suggest that dissolved iron concentrations in oxic surface water and wastewater are typically higher than those of dissolved sulfide, the actual percentages of dissolved sulfide present as H_2S/HS^- are expected to generally be much less than 15%. This means that the H_2S/HS^- concentrations measured in water are likely overestimations of un-ionized hydrogen sulfide.

Another potential source of uncertainty relates to the technical difficulties associated with sampling and accurately measuring aqueous concentrations of dissolved sulfides in environmental media. For instance, when method detection limits are acceptable, there is the challenge of avoiding loss of sulfide from sampled water prior to chemical analysis (for example, by volatilization, oxidation, or adsorption to container walls). As a result, it is unknown whether concentrations in these studies were underestimated.

While there are sufficient environmental concentration data for hydrogen sulfide (measured as dissolved sulfide) in Canadian surface waters and effluents, there are still some limitations in the available data set. For example, although very high sulfide concentrations were measured in the outflow from a bioreactor at an Alberta coal mine, no information was available on concentrations in nearby surface water. Furthermore, data on dissolved sulfide concentrations in surface water downstream of oil sands operations were only identified at one location in Alberta. It is not clear how representative this location is or how sulfides are released to water from the oil sands facility. In addition, most of the data for surface water associated with pulp and paper mills were for facilities located in the United States and may not accurately represent Canadian facilities. There are also limited reported incidental data available for aquatic media. One site in southern Ontario reported discharge of hydrogen sulfide from an artesian well at levels of greater than 110 mg/L over a month-long period.

Regarding the assessment of exposure of terrestrial organisms, there are large amounts of credible short-term (1-hour) monitoring data available on ambient concentrations in Canadian air near anthropogenic sources of release.

Incidental releases of hydrogen sulfide have been shown to be associated with inactive oil and gas wells. Data characterizing a limited number of sites in southern Ontario indicate that these sources may generate air concentrations that persist for several hours up to and exceeding 100 ppm. Alone, these sites are considered to under-represent the potential scope of the issue given the large number of inactive oil and gas wells (for example, at least 11 000 in Ontario alone).

Longer-term (1-month) exposure information is less abundant, and consequently, there is greater uncertainty associated with the estimation of the maximum long-term terrestrial PECs. The assessment factors used to derive the terrestrial PNECs from the CTVs are considered adequate to address uncertainties related to the limitations of the toxicity data available. The lowest assessment factor of 2, used to derive a long-term PNEC for plants of 70 $\mu g/m^3$, is considered justified in view of the stimulatory effects of hydrogen sulfide observed in many plant species when exposed at low levels.

8. Potential to cause harm to human health

Exposure to sodium bisulfide or sodium sulfide may occur from industrial or commercial releases primarily to water (see section 5). These substances are expected to dissociate in water to form bisulfide, sulfide anions, and hydrogen sulfide, and are expected to undergo oxidation in air to other sodium salts. Additionally, soluble sulfides including sodium sulfide and sodium bisulfide are reported to be rapidly and completely hydrolyzed in the body to produce hydrogen sulfide. Therefore, the focus of the human health assessment for substances in this group is on hydrogen sulfide.

8.1 Exposure assessment

8.1.1 Environmental media

Hydrogen sulfide is a diprotic acid in equilibrium with two anionic forms, namely the bisulfide (HS^-) and sulfide (S^{2-}) ions. At pH values relevant to environmental waters (for example, pH of 6.0 to 9.0), hydrogen sulfide and the bisulfide anion will be the predominant species. Alkali metal salts, such as sodium bisulfide ($Na(SH)$) and sodium sulfide (Na_2S), are readily soluble in water and have the potential for release to environmental waters from industrial processes. If released to water, sodium bisulfide and sodium sulfide would dissociate to form the anions HS^- and S^{2-}, respectively. These anions would then enter the natural sulfur cycle and, depending on the pH, result in the formation of hydrogen sulfide via the equilibrium mentioned above. Therefore, the focus of this assessment of environmental exposure is on hydrogen sulfide (H_2S).

Also, as noted earlier, 60% to 90% of hydrogen sulfide in the atmosphere is estimated to originate from natural sources (US EPA 1993; Watts 2000). In addition, a comparison of the total import volume of sodium sulfides in Canada for the 2015 calendar year (9 217 213 kg) with the total volume of hydrogen sulfide manufactured (including incidentally) in the 2000 calendar year (8 670 000 000 kg) suggests that any releases resulting from the commercial use of either of the two sulfides of sodium would contribute only a minor fraction to total hydrogen sulfide levels in the environment (Environment Canada 2004a; StatsCan 2015).

Hydrogen sulfide is part of the natural sulfur cycle and has many natural sources, including volcanoes, sulfur springs, and petroleum deposits. It has been detected in well water in Canada and in groundwater in other countries, within close proximity to pulp and paper mills and petroleum refineries (US EPA 2003; ATSDR 2006).

While not quantified, hydrogen sulfide has been detected in tap water in some homes, resulting in a musty or rotten egg smell. Although hydrogen sulfide can be found in water under specific environmental conditions, the majority is released to air, and inhalation of ambient air is expected to be the primary route of human exposure.

Empirical data on measured concentrations of hydrogen sulfide in ambient air from continuous air monitoring are presented in section 6.1.1 Environmental distribution and persistence—air, and in Appendix C. Based on these data, the value of 1 ppb (1.4 µg/m^3), reported as the average concentration found in urban areas away from point sources (Alberta Environment 2000a), is considered to be a conservative representation of the potential concentration to which the general population could be exposed in an urban environment. Numerous measurements of hydrogen sulfide concentrations in ambient air near commercial activities that are known point sources have been reported, constituting a large data set of millions of samples collected over several decades. These commercial activities include pulp and paper mills, oil and gas operations, natural gas processing facilities, petroleum refineries, and livestock farms.

The highest 99th percentile ambient air concentration reported from the available data is 31 ppb (43.4 µg/m^3). This value is based on measured concentrations near a Canadian pulp and paper mill (WGAQOG 2000) and on samples collected hourly and continuously over four years, between 1994 and 1998. The range of all 99th percentile concentrations measured near point sources in Canada and reported in the literature falls within the range of concentrations measured near this pulp and paper mill at the time; therefore, 31 ppb is considered to be an upper-bound representation of the potential hydrogen sulfide concentration to which the general population could be exposed while living near a known point source. The range of concentrations of 1 ppb to 31 ppb (1.4 µg/m^3 to 43.4 µg/m^3) is used in the risk characterization.

8.1.2 Incidental exposure

In addition to ambient air concentrations reported from continuous monitoring described above, information on a number of incidents during which high concentrations or spikes of hydrogen sulfide were released in the proximity of urban or community areas in Canada were collected via input received from provincial and municipal jurisdictions, mainly in Ontario. Details of these data are provided in Appendix D.

The information indicates that hydrogen sulfide can be released from inactive oil and gas wells (see Appendix A for additional information on the different statuses of inactive wells, that is, suspended, abandoned, or orphaned). Hydrogen sulfide can leak from inactive wells, potentially due to degraded structural integrity, which may result in incidental exposure of the general population depending on the location of the well, proximity to inhabited areas, and certain environmental conditions (for example, wind conditions).

In one incident in southern Ontario (in the vicinity of the City of Hamilton, and Haldimand and Norfolk Counties), levels of hydrogen sulfide of up to 6 ppm were measured on a private property in 2017, several meters from the dwelling, near the barn of the owner. The source of hydrogen sulfide was one of several inactive oil and gas wells on the property (personal communication, email from the Ministry of Environment and Climate Change, Government of Ontario, to the Existing Substances Risk Assessment Bureau, Health Canada, dated April 2018; unreferenced).

In another incident in the same areas of Haldimand and Norfolk Counties, point-in-time readings were gathered over the course of a year between early 2018 and early 2019 from monitors near multiple residences near which a gas well was found to be releasing hydrogen sulfide. The data collected demonstrated sporadic and irregular spikes in hydrogen sulfide levels that could persist for several hours, with peak levels as high as 180 ppm (personal communication, emails from the Haldimand-Norfolk Health and Social Services, to the Existing Substances Risk Assessment Bureau, Health Canada, dated February 2019, unreferenced).

Additional data from inspection reports by the Ontario Ministry of Natural Resources and Forestry (MNRF) have demonstrated a number of occurrences for which high levels of hydrogen sulfide have been recorded during inspections of wells located in southern Ontario. Of 65 point-in-time measurements of hydrogen sulfide reported from 2010 onwards, there were 59 reports for which hydrogen sulfide levels were greater than or equal to 2 ppm. Of these 59 reports, 24 reported levels of between 10 ppm and 100 ppm, and 16 reported levels of 100 ppm or greater. The 43 inspected wells were located throughout southern Ontario in both rural and urban settings, including residential communities (personal communication, email from the MNRF, Government of Ontario, to the Existing Substances Risk Assessment Bureau, Health Canada, dated June 6, 2018; unreferenced). As indicated in Appendix A, there are over 9000 abandoned historic oil and gas wells in Ontario, with over 1500 suspended or orphaned.

Inactive wells also exist in other Canadian provinces. It is estimated that there are 261 000 inactive wells among the western provinces of Alberta, Saskatchewan, and British Columbia (Appendix A). The Government of Alberta reports that, as of 2022, there are around 7700 wells designated as orphaned by the Alberta Energy Regulator (Alberta 2022). It is also noted that there are over 80 000 abandoned wells in Alberta. The Government of Saskatchewan (2022b) has noted that the province currently has approximately 67 500 inactive oil and gas wells, of which about 42 000 are abandoned and about 500 are orphan sites requiring work.

Information collected from the Ontario Ministry of Environment Conservation and Park's (MOECP) Spills Action Centre (SAC) (data submitted from 2005 to 2018) also includes reports of incidental exposure of the general population to hydrogen sulfide. Among the data collected, there were six incidents for which levels of hydrogen sulfide were measured in close proximity to neighbouring communities in southern Ontario (London, Windsor, Sarnia, Hamilton), with reported levels ranging from 6 ppm to as high as 100 ppm (MOECP 2019). In four of these incidents, it was suspected that hydrogen sulfide had been released from historic oil and gas or artesian wells.

Elsewhere in Canada, an occurrence of high levels of hydrogen sulfide on a residential property in 2012 resulted in an individual experiencing severe health effects (vomiting; burning eyes) following acute exposure to levels greater than 100 ppm of hydrogen sulfide, according to a media report from Oxbow, Saskatchewan (Cribb 2017).

8.2 Health effects assessment

Limited information on the toxicity of sodium sulfide and sodium bisulfide has been identified in the literature. However, soluble sulfides (which include sodium sulfide and sodium bisulfide) are reported to be rapidly and completely hydrolyzed in body fluids to produce hydrogen sulfide. As a result, there are no toxicological distinctions between them and hydrogen sulfide in terms of their systemic effects and toxicokinetic profile (Health Canada 1987), and this section will focus on the health effects of hydrogen sulfide. The available toxicity studies conducted specifically with sodium sulfide and sodium bisulfide are summarized at the end of this section.

Appendix B contains additional details on the key health effects studies for hydrogen sulfide that were reviewed for this assessment.

8.2.1 Hydrogen sulfide

8.2.1.1 Toxicokinetics

Hydrogen sulfide is produced endogenously as part of normal biological function, playing a role in regulating blood pressure, body temperature, vascular smooth muscle, cardiac function, and cerebral ischemia as well as in modulating the hypothalamic-pituitary-adrenal axis. It is produced by the brain, liver, heart, and gastrointestinal tract (Kimura 2002; Kamoun 2004; Linden et al. 2010). After exposure, hydrogen sulfide is absorbed rapidly by the lungs and is widely distributed throughout the body (US EPA 2003; ATSDR 2006). Sulfide levels were detected in the liver, blood, brain, lungs, spleen, and kidneys of humans who had been accidentally exposed (Kimura et al. 1994; Imamura et al. 1996) as well as in experimentally exposed animals (Nagata et al. 1990; Kohno et al. 1991). Similar distribution patterns were observed in humans and in experimental animals. The concentration of sulfide was highest in the heart, whereas the level in the brain was comparable to levels in the lung, liver, kidney, and spleen.

Hydrogen sulfide can be metabolized by oxidation (US EPA 2003; ATSDR 2006). Additionally, methylation and conjugation with metalloproteins are two postulated pathways. The major metabolic pathway is oxidation of the sulfide, firstly to thiosulfate and then to sulfate (Bartholomew et al. 1980; Beauchamp et al. 1984). The major oxidation site is the liver, and excretion of the metabolites occurs primarily through the kidneys. One of the postulated metabolic pathways is methylation. Weisiger et al. (1980) found that hydrogen sulfide can be methylated by the intestinal mucosa of Sprague-Dawley rats *in vitro* (Weisiger et al. 1980). This process is catalyzed by thiol *S*-methyltransferase, which is thought to be a minor metabolic pathway as the methylation rate is expected to be significantly slower than the oxidation rate (Levitt et al. 1999). Another postulated metabolic pathway is reaction of hydrogen sulfide with metalloproteins. This pathway was postulated primarily on the basis of limited evidence (Smith and Abbanat 1966; Beauchamp et al. 1984).

8.2.1.2 Toxicodynamics

Several mechanisms of hydrogen sulfide toxicity have been proposed for exposure at high concentrations. Some investigators have suggested the involvement of a neurotoxic pathway. Others have suggested that toxicity is triggered in the lung at the site of contact. One of the postulated mechanisms involve the inhibition of cytochrome oxidase, which is a critical enzyme for cellular mitochondrial respiration (Chance and Schoener 1965; Nicholls 1975; Smith et al. 1977). Inhibition of cytochrome oxidase would lead to blockage of oxidative metabolism. Because the brain and the nervous system have a high oxygen demand, blockage of oxidative metabolism can lead to respiratory arrest (Warenycia et al. 1989). Other investigators have suggested that the direct inhibition of cytochrome oxidase in the lung tissues is the primary pathway leading to respiratory arrest (Khan et al. 1990). Another postulated mechanism is related to the effects on nerve endings. Based on studies in rats, Almeida and Guidotti (1999) suggested that the hydrosulfide anion can act on nerve endings of the pulmonary vagi, paralyzing the ventilatory centre in the brain. The hydrosulfide anion can also act directly on neurons in the ventilatory centre in the brain *in vitro,* interfering with neurotransmission (Kombian et al. 1993).

8.2.1.3 Genotoxicity and carcinogenicity

No genotoxicity or carcinogenicity classifications by other national or international regulatory agencies were identified. No long-term or carcinogenicity studies with hydrogen sulfide were identified. Ames tests in *Salmonella typhimurium* strains TA97, TA98, and TA100, with and without metabolic activation, indicated no mutagenic potential (Hughes et al. 1984). Mixed results were observed in *in vitro* comet assays depending on cell types and whether the DNA repair system was active. Positive results were observed in human small intestine cells (Attene-Ramos et al. 2010) but not in Chinese hamster ovary (CHO) cells nor human colonic cancer cells when the DNA repair system was active. When DNA repair was inhibited, positive results were observed in both CHO cells and human colonic cancer cells (Attene-Ramos et al. 2006).

8.2.1.4 Odour threshold

Hydrogen sulfide is very odorous, with a low olfactory threshold ranging from less than 0.01 ppm to 0.3 ppm (0.014 mg/m^3 to 0.42 mg/m^3). There is some uncertainty associated with determining a specific odour threshold as it varies with individual sensitivity (WHO 2000; Greenberg et al. 2013). The median odour detection threshold for hydrogen sulfide reported by Amoore and Hautala (1983), on the basis of a compilation of 25 published reports of odour threshold, was 0.008 ppm (0.011 mg/m^3). Amoore and Hautala (1983) also reported that a 250-fold range in odour sensitivities would be likely in a group of 100 observers. Although hydrogen sulfide can be perceived as a nuisance in community settings because of its smell, there is insufficient evidence that it causes adverse health effects at these low levels (Logue et al. 2001; Horton et al. 2009).

After prolonged exposure, olfactory fatigue can occur when the sensory system has adapted to the smell of hydrogen sulfide. At high concentrations (100 ppm to 200 ppm [140 mg/m^3 to 280 mg/m^3]), hydrogen sulfide paralyzes the olfactory nerve, preventing odour detection (Reiffenstein et al. 1992; Guidotti 1994).

8.2.1.5 Ocular effects

In a study by Savolainen (1982), a threshold for human eye irritation was observed at 10 ppm to 20 ppm (15 mg/m^3 to 30 mg/m^3), and serious eye damage was observed at 50 ppm to 100 ppm (70 mg/m^3 to 140 mg/m^3). The WHO air quality guideline value for hydrogen sulfide is 0.15 mg/m^3 (0.11 ppm) for an average concentration over 24 hours based on eye irritation (WHO 2000; IPCS 2003). In occupational settings, workers exposed to 10.71 ppm to 20.71 ppm (15 mg/m^3 to 29 mg/m^3) hydrogen sulfide for 6 to 7 hours have reported eye irritation (IPCS 1981). Riffat et al. (1999) reported that exposure to hydrogen sulfide at concentrations greater than 50 ppm (70 mg/m^3) for 1 hour can severely damage eye tissue. In a community near a paper mill where an annual mean concentration of 6 µg/m^3 hydrogen sulfide was recorded, with daily peak concentrations up to 100 µg/m^3, eye irritation was reported 12 times more frequently than in communities without exposure (Jaakkola et al. 1990). However, co-exposure to methyl mercaptan and methyl sulfide also occurred. In an occupational survey, Vanhoorne et al. (1995) noted that a significantly higher number of eye irritation complaints were reported by workers exposed to hydrogen sulfide concentrations greater than 5 mg/m^3. However, the workers were also exposed to carbon disulfide.

8.2.1.6 Respiratory effects

In laboratory animals following acute inhalation exposure, the lowest LOEC was 10 ppm (14 mg/m^3), as identified in Dorman et al. (2002) and Lopez et al. (1987). In the Dorman et al. (2002) study, the LOEC was based on a significant decrease in cytochrome oxidase activity in the liver of Sprague-Dawley rats exposed to 0, 10, 30, 80, 200, or 400 ppm (0, 14, 42, 110, 280, or 560 mg/m^3) hydrogen sulfide for 3 hours. In the Lopez et al. (1987) study, the LOEC was based on a significant transient increase in the cellularity of nasal lavage fluid, which returned to original levels at 20 hours post-exposure, in male Fischer 344 rats exposed to 0, 10, 200, or 400 ppm (0, 14, 280, or 560 mg/m^3) hydrogen sulfide for 4 hours.

With regard to short-term repeated inhalation exposure, the lowest LOEC was 10 ppm (14 mg/m^3) (no-observed-effect-level [NOEC] = 1 ppm or 1.4 mg/m^3) on the basis of significantly reduced cytochrome oxidase activity in lung mitochondria in male Fischer 344 rats exposed to 0, 1, 10, or 100 ppm (0, 1.4, 14, or 140 mg/m^3) hydrogen sulfide 8 hours/day, 5 days/week, for 5 weeks (Khan et al. 1998).

For longer-term inhalation exposure, a no-observed-adverse-effect concentration (NOAEC) of 10 ppm (14 mg/m^3) was identified with a lowest-observed-adverse-effect concentration (LOAEC) of 30 ppm (42 mg/m^3) in Brenneman et al. (2000) and Dorman et al. (2004). Brenneman et al. (2000) exposed male Sprague-Dawley rats to 0, 10, 30, or 80 ppm (0, 14, 42, or 110 mg/m^3) hydrogen sulfide for 6 hours/day, 7 days/week, for 10 weeks. The LOAEC was based on mild to moderate olfactory neuron loss and basal cell hyperplasia in the olfactory mucosa. The Dorman et al. (2004) study was a reassessment of the nasal and lung histopathology from the Chemical Industry Institute of Toxicology (CIIT 1983a,b,c) studies. In the CIIT (1983a,b,c) studies, Fischer 344 rats, Sprague-Dawley rats, and B6C3F1 mice were exposed to 0, 10.1, 30.5, or 80 ppm (0, 14, 42, or 110 mg/m^3) hydrogen sulfide for 6 hours/day, 5 days/week, for 90 days. A LOEC of 80 ppm was identified primarily on the basis of decreased food consumption and body weights. Dorman et al. (2004) reassessed the nasal and lung histopathology from the CIIT (1983a,b,c) studies and identified a significant increase in the incidence of olfactory neuronal loss at 30 ppm and higher in all animals except male Sprague-Dawley rats. For male Sprague-Dawley rats, a significant olfactory neuronal loss was observed at 80 ppm. No chronic inhalation studies were identified. IPCS (2003), US EPA (2003), and ATSDR (2006) used the Brenneman et al. (2000) study to derive a medium-term tolerable concentration, an inhalation reference concentration, and an intermediate-duration inhalation minimal risk level, respectively.

Dorman et al. (2004) noted that there are significant differences between the breathing styles and nasal anatomy of rodents and humans. Rodents such as mice and rats are obligatory nasal breathers, and a large portion of the rodent nasal cavity (50%) is lined by olfactory mucosa relative to humans (10%). In addition, the structure of the nasal cavity in rodents allows a greater surface area to be exposed to inhaled chemicals at a slower speed of air flow for more efficient chemical uptake than in humans. The combination of these factors increases the probability that a chemical inhaled through the rodent nose will deposit in the olfactory mucosa for a longer duration that is sufficient to cause toxicity and which could, over time, result in irreversible lesions.

Respiratory effects in human subjects have also been studied.

The Bhambhani research group conducted several studies on the effects of hydrogen sulfide on healthy human subjects and demonstrated that exposure for 15 to 30 minutes

via “oral inhalation” during various exercise levels to concentrations of up to 10 ppm (14 mg/m^3) did not result in adverse effects. In two studies, healthy volunteers were exposed to 0, 0.5, 2, or 5 ppm (0, 0.7, 2.8, or 7 mg/m^3) hydrogen sulfide via oral inhalation during graded cycle exercise until exhaustion (Bhambhani and Singh 1985, 1991). In the 1985 study, 16 male subjects were ranked on the basis of their relative maximum oxygen uptake and categorized into “high fit” and “low fit” groups. A significant decrease in respiratory exchange ratio (RER) was observed at 0.5 ppm in the “low fit” group and at 5 ppm in the “high fit” group at the maximum exercise level. Female subjects were not classified into fitness groups due to small group size, and a significant reduction in RER was observed at 5 ppm at all exercise levels. In Bhambhani and Singh (1991), a significant decrease in RER was observed at 2 ppm in 16 healthy male volunteers exercising at the maximum level. Although statistically significant changes in RER were observed at 2 ppm, no significant pulmonary effects were observed by the authors. The authors concluded that healthy individuals can safely exercise at their maximum metabolic rates while exposed to 5 ppm hydrogen sulfide.

Bhambhani and co-workers later focused on the health effects at 50% of a predetermined maximal aerobic exercise level. No significant physiological or pulmonary effects were observed when healthy volunteers were exposed to 0 ppm or 5 ppm (0 mg/m^3 or 7 mg/m^3) hydrogen sulfide for 30 minutes (Bhambhani et al. 1994, 1996b). Bhambhani et al. (1996a, 1997) further tested the effect of hydrogen sulfide at 10 ppm (14 mg/m^3) after 15 or 30 minutes of exposure. In the group exposed for 15 minutes, no significant effects on pulmonary functions were observed (Bhambhani et al. 1996a). In the group exposed for 30 minutes, a significant decrease in oxygen uptake and a significant increase in the RER and blood lactate levels were observed (Bhambhani et al. 1997). From these studies, the authors concluded that oral inhalation of hydrogen sulfide up to 10 ppm (14 mg/m^3) did not significantly alter pulmonary function in healthy individuals.

Participants in the above-mentioned studies were exposed while exercising to exhaustion, a scenario that is representative of an occupational setting but not of the general population’s typical activity levels. However, it does indicate that at typical activity levels, exposure to up to 10 ppm (14 mg/m^3) hydrogen sulfide would not compromise pulmonary function in healthy individuals.

In an earlier study, Jäppinen et al. (1990) examined possible respiratory effects associated with hydrogen sulfide in 26 male pulp mill workers and 10 asthmatic volunteers. In the cohort of non-asthmatic mill workers exposed to hydrogen sulfide levels ranging from 1 ppm to 11 ppm in the workplace, standard histamine challenges were performed after a holiday or one day away from work and at the end of the work day. When comparing responses obtained after a holiday or one day away from work, with responses obtained at the end of the work day, no statistically significant effects on respiratory function or bronchial reactivity were observed. In the volunteer study, the asthmatic volunteers were exposed to 2 ppm (2.8 mg/m^3) hydrogen sulfide (one-fifth of the Finnish maximum allowable workplace concentration of 10 ppm) for 30 minutes in an exposure chamber.

In this part of the study, respiratory measurements were compared before and after exposure. When the asthmatic subjects were exposed to 2 ppm hydrogen sulfide, 3 out of 10 hydrogen sulfide-exposed subjects reported headaches, and measurement of airway resistance increased. As a group, airway resistance increased by 26.3% on average, and specific airway conductance decreased by an average of 8.4%, which, although not statistically significant, is considered biologically significant. Thus, the effect level for increased airway resistance in asthmatics was 2 ppm (2.8 mg/m^3) hydrogen sulfide.

Both the ATSDR (2006) and IPCS (2003) used the Jäppinen et al. (1990) study to derive the acute-duration inhalation minimal risk level and the short-term tolerable concentration, respectively, while acknowledging the limitations of the study. In February 2010, the American Conference of Governmental Industrial Hygienists (ACGIH) lowered the recommended workplace threshold limit value (TLV, 8 h/day) for hydrogen sulfide from 10 ppm to 1 ppm (ACGIH 2010).

More recently, Bates et al. (2013) examined any potential association between chronic exposure to hydrogen sulfide from geothermal sources and self-reported asthma and asthma symptoms in a population living in Rotorua, New Zealand. A total of 1637 men and women (aged 18 to 65) who had resided in Rotorua for at least 3 years participated. Participants were grouped into 4 quartiles (0 ppb to 10 ppb, 11 ppb to 20 ppb, 21 ppb to 30 ppb, and 31 ppb to 64 ppb). No increased asthma risk was found in association with hydrogen sulfide exposure.

Campagna et al. (2004) studied the association between hydrogen sulfide exposure and hospital visits for asthma and similar respiratory diseases in two populations in Nebraska, USA, from 1998 to 2000. In the study, hospital records from South Sioux City and Dakota City were examined for patients diagnosed with asthma and matched with ambient and indoor hydrogen sulfide levels the day before hospital admission. Concentrations were categorized as “high” if at least one of the daily 30-min. rolling averages were ≥30 ppb or “low” if all 30-min. rolling averages were <30 ppb. During the 29-month study period, 5009 hospital visits were for respiratory diseases, including 455 for asthma, with children accounting for one-third of visits. A positive association was found between adult and children hospital visits for respiratory disease, including asthma, and “high” (≥30 ppb) hydrogen sulfide levels on the previous day, compared to a day with “low” (<30 ppb) levels. While the exact levels of hydrogen sulfide detected are not presented in the study, an earlier study (Inserra et al. 2002) showed that monthly rolling averages of hydrogen sulfide in the same populations ranged from 2 ppb to over 90 ppb. In addition, hydrogen sulfide monitors in parts of South Sioux City and all parts of Dakota City detected hydrogen sulfide levels that were consistently greater than 30 ppb, where levels met or exceeded the 90 ppb detection limit 46 times over a 9-month period.

8.2.1.7 Neurological effects

Effects of hydrogen sulfide exposure on the behaviour of experimental animals were examined in several studies. In rats exposed to 100 ppm or 200 ppm (139 mg/m^3 or 280 mg/m^3) hydrogen sulfide for 1 to 2 hours, a LOAEC of 200 ppm was observed on the basis of a significant decrease in discriminated avoidance response (Higuchi and Fukamachi 1977). The lowest NOAEC following short-term inhalation exposure of test animals identified in the literature was 30 ppm (42 mg/m^3), with a LOAEC of 80 ppm (110 mg/m^3) on the basis of a significant reduction in spontaneous motor activity and body temperature in rats exposed (nose-only) to 0, 30, 80, 200, or 400 ppm (0, 42, 110, 280, or 560 mg/m^3) hydrogen sulfide for 3 hours/day for 5 consecutive days (Struve et al. 2001). Struve et al. (2001) analyzed the brains for catecholamines and found that there were no exposure-related decreases in brain catecholamine levels in the striatum, hindbrain, or hippocampus following exposures up to 400 ppm. In addition, learning and memory were not impaired following exposures (whole-body) of up to 80 ppm hydrogen sulfide for 5 days, as evaluated using a modification of the Morris water maze protocol.

Fiedler et al. (2008) conducted a human exposure study with 74 healthy subjects (35 females, 39 males) exposed to 0.05, 0.5, and 5 ppm (0.07, 0.7, and 7 mg/m^3) hydrogen sulfide in a random order for 2 hours over 3 weeks in an exposure chamber. The authors reported that although some symptoms, such as decreased odour detection and increased irritation and anxiety, were statistically different with exposure over time, the magnitude of these changes was minor. A significant decline in cognitive recall through auditory verbal learning was observed at all exposure levels over time, which the authors suggested could be due to fatigue. The authors noted that a threshold effect was not consistently observed for other neurobehavioural measures as no significant effects on other sensory or cognitive measures, such as complex reaction time, were observed in a dose-response manner. Thus, Fiedler et al. (2008) reported that up to 5 ppm hydrogen sulfide had statistically significant effects of minor magnitude in healthy individuals. However, according to the authors, the exposure dose range was within the range of anticipated general population exposures; therefore, they could not identify a no-adverse-effect level.

In epidemiological studies, the Kilburn research group studied the neurological effects of humans exposed to hydrogen sulfide (Kilburn and Warshaw 1995; Kilburn 1997, 1999, 2003, 2012). Neurobehavioural effects were evaluated in individuals who had been exposed for various lengths of time to low-level environmental hydrogen sulfide concentrations. A number of neurobehavioural effects, possibly associated with hydrogen sulfide exposure, were identified, which included alterations in balance, visual fields, choice reaction time, colour discrimination, grip strength, and delayed verbal recall. In some cases, exposure levels were not reported; in others, exposure levels were estimated. Some subjects were also concurrently exposed to other substances.

The same subjects who live in the city of Rotorua, New Zealand, with chronic exposure to hydrogen sulfide from geothermal sources as described in Bates et al. (2013), were also administered a series of neuropsychological tests (Reed et al. 2014) to examine any association between chronic, low-level exposures to hydrogen sulfide and cognitive function. These neuropsychological tests evaluated attention, memory, psychomotor speed, fine motor function, and mood. Overall, no association was identified between hydrogen sulfide exposure and cognitive function in this population residing in Rotorua with chronic, low-level exposure to hydrogen sulfide.

In human case studies, most of which were occupational or accident-related, concentrations and durations of exposure to hydrogen sulfide were usually not quantified, and co-exposure to other chemicals was often the case. Some neurological effects observed included coma, seizures, dizziness, dementia, decreased ability to communicate, decreased attention and concentration, memory impairment, impaired visual perception and coordination, impaired motor function, ataxia, cerebral atrophy, and irritability (Allyn 1931; Ahlborg 1951; McDonald and McIntosh 1951; Spolyar 1951; Breysse 1961; Milby 1962; Krekel 1964; Adelson and Sunshine 1966; Thoman 1969; Simson and Simpson 1971; Burnett et al. 1977; Osbern and Crapo 1981; Hagley and South 1983; Beauchamp et al. 1984; Arnold et al. 1985; Audeau et al. 1985; Deng and Chang 1987; Luck and Kaye 1989; Wasch et al. 1989; NIOSH 1991; Parra et al. 1991; Tvedt et al. 1991a,b; Kilburn 1993; Snyder et al. 1995; Hall and Rumack 1997; Watt et al. 1997).

8.2.1.8 Reproductive and developmental effects

No reproductive or developmental classifications by other national or international regulatory agencies were identified. A NOEC of 80 ppm (110 mg/m^3) was identified in male and female Sprague-Dawley rats exposed to 0, 10, 30, or 80 ppm (0, 14, 42, or 110 mg/m^3) hydrogen sulfide for 6 hours/day, 7 days/week (Dorman et al. 2000). No reproductive toxicity was observed in the exposed male and female F_0 rats. No developmental toxicity was observed in the pups. There were no significant effects observed in pup growth, development, behavioural performance, or neuropathology. Behavioural tests included motor activity, passive avoidance, functional observation battery, and acoustic startle response.

In terms of neurodevelopmental effects, Hannah and Roth (1991) examined the perinatal effect of hydrogen sulfide on developing cerebellar Purkinje cells in rat pups. A LOEC of 20 ppm (28 mg/m^3) was identified on the basis of significant alterations in the architecture and growth characteristics of the Purkinje cell dendritic fields in pups when pregnant Sprague-Dawley rats were exposed to 0, 20, or 50 ppm (0, 28, or 70 mg/m^3) hydrogen sulfide for 7 hours/day from gestation day 5 to postnatal day 21. However, the US EPA (2003) questioned whether these alterations could be seen as adverse as “the effects reported are highly selective and could be due to environmental factors not directly related to exposure, including variability resulting from the restricted sampling technique (that is, one Purkinje cell per pup).”

Developmental neurochemical changes were examined by Skrajny et al. (1992). A LOEC of 20 ppm (28 mg/m^3) was identified on the basis of significantly increased serotonin levels in the frontal cortex in exposed pups when pregnant rats were exposed to 0, 20, or 75 ppm (0, 28 or 105 mg/m^3) hydrogen sulfide for 7 hours/day from gestation day 5 to postnatal day 21 (Skrajny et al. 1992). No evidence is available to suggest that changes in Purkinje cell dendritic fields or neurotransmitter levels would lead to toxicological alterations in neurobehavioural performance.

8.2.2 Sodium sulfide and sodium bisulfide

Limited data are available for sodium sulfide and sodium bisulfide genotoxicity. Sodium sulfide was not mutagenic in bacterial mutation assays using *Salmonella typhimurium* strains TA98, TA100, TA1535, and TA1537, with and without metabolic activation (conducted according to the Organisation for Economic Co-operation and Development Test Guideline [OECD TG] 471). Negative results were also observed in a mammalian lymphoma cell mutation assay (OECD TG 476) using mouse lymphoma L5178Y cells exposed to sodium sulfide at doses up to 781 µg/ml, with and without metabolic activation (ECHA 2019a; NICNAS 2016).

One *in vivo* assay was identified for sodium sulfide. Negative results were noted for micronucleus induction in bone marrow cells of NMRI mice administered sodium sulfide intraperitoneally at doses of 24, 48, or 96 mg/kg bw (ECHA 2019a; NICNAS 2016).

No carcinogenicity studies were identified, with the exception of a limited study conducted with sodium sulfide. In this study, Charles River CD rats (n=26/sex/dose) were administered sodium sulfide in water by gavage at doses of 9 mg/kg bw/day and 18 mg/kg bw/day, in the presence or absence of 1% thyroid extract, twice a week for 56 weeks and 2 to 3 times a week for an additional 22 weeks (for a total of 78 weeks). A significant association between mortality and dose was noted in treated males without the 1% thyroid extract. However, this association was not found in the other group treated with sodium sulfide and the thyroid extract. Although females treated with sodium sulfide and thyroid extract exhibited a higher mortality, the significance was not specified. The results were termed “ambiguous” by the authors. No evidence for the carcinogenicity of sodium sulfide was found in this study (Weisburger et al. 1981; Health Canada 1987).

Limited information is available for Na_2S and NaSH repeated dose toxicity. In one study, Yorkshire pigs (n=144) were fed diets containing 0, 225, or 450 ppm Na_2S (equivalent to 0, 6.75, or 13.5 mg/kg bw/day using a dose conversion by Health Canada 1994) for 104 days. No signs of toxicity were observed (Cromwell et al. 1978).

Under physiological pH, these substances will dissociate into hydrogen sulfide anions (HS-) and hydrogen sulfide. Under acidic conditions (such as in the stomach), the formation of hydrogen sulfide is more important (Meyer et al. 1983; NICNAS 2016). Adverse health effects observed after repeated oral exposure cannot be ruled out (NICNAS 2016).

No dermal or inhalation studies were identified for Na_2S or NaSH. Repeated exposure to these chemicals could lead to lung effects and nasal damage from the release of hydrogen sulfide (NICNAS 2016).

No reproductive or developmental studies were identified for sodium sulfide or sodium bisulfide. On the basis of the available data for hydrogen sulfide, no reproductive or developmental toxicity is expected for these two substances.

Considering the high basicity of the sulfide anions, sulfides such as sodium sulfide and sodium bisulfide are expected to have severe irritation/corrosive properties (NICNAS 2016). Sodium bisulfide is reported as a strong irritant to skin and mucous membranes (HSDB 2003). A 30% sodium bisulfide solution applied to the conjunctival sac of the eyes of 6 Himalayan rabbits caused irreversible eye damage (ECHA 2019b).

8.3 Characterization of risk to human health

8.3.1 Ambient air monitoring

Sodium bisulfide and sodium sulfide, if released to the environment via commercial activities, are anticipated to result in the formation of the sodium cation and the bisulfide or sulfide anions, respectively. Since such anions are in equilibrium with hydrogen sulfide, sodium bisulfide and sodium sulfide are expected to contribute to total hydrogen sulfide levels in the environment (albeit to a minor extent relative to other sources). If human exposures to undissociated sodium bisulfide or sodium sulfide were to occur, either salt would rapidly and completely hydrolyze in bodily fluids, resulting in the formation of hydrogen sulfide. No specific additional hazard is associated with either salt beyond that posed by hydrogen sulfide (Health Canada 1987). This section will therefore focus on characterizing the human health risk associated with exposure to hydrogen sulfide.

Hydrogen sulfide is produced endogenously at low concentrations as part of normal biological function and plays a regulatory role in mammalian physiology; it is thus normally present in mammals, including humans (Mancardi et al. 2009). No mutagenicity or carcinogenicity classifications by other national or international regulatory agencies were identified, and no data were identified to suggest that hydrogen sulfide is mutagenic or carcinogenic.

The predominant route of exposure to hydrogen sulfide for Canadians is through inhalation of ambient air. Hydrogen sulfide present in ambient air comes from natural and anthropogenic sources, and a review of the available data on continuous air monitoring indicates that a representative upper-bounding range of ambient air concentrations to which the general population would be exposed is 0.001 ppm to 0.031 ppm (0.0014 mg/m^3 to 0.0434 mg/m^3). The lowest value of this range represents the overall average concentration measured in an urban area presumed to be located away from major anthropogenic sources (Alberta Environment 2000a);

the highest value of the range is the highest of all 99th percentile concentrations derived for each of 64 sites monitored near Canadian pulp and paper mills (WGAQOG 2000).

Odour threshold

Hydrogen sulfide is very odorous, with a low olfactory threshold that ranges from less than 0.01 ppm to 0.3 ppm (0.014 mg/m^3 to 0.42 mg/m^3). Although hydrogen sulfide can be perceived as a nuisance in a community setting because of its smell, there is insufficient evidence that it causes adverse health effects at these low levels (Logue et al. 2001; Horton et al. 2009).

Because olfactory nuisance is not considered to be adverse for the purpose of this assessment, it is not taken into account in terms of characterizing risk for hydrogen sulfide.

Ocular effects

The critical LOEC for ocular effects is 10 ppm to 20 ppm (15 mg/m^3 to 30 mg/m^3), which is based on the human eye irritation threshold reported in Savolainen (1982). The WHO air quality guideline value for hydrogen sulfide was derived on the basis of eye irritation observed in the Savolainen (1982) study. Comparison of this LOEC with the upper-bounding range of ambient air concentrations of 0.001 ppm to 0.031 ppm (Alberta Environment 2000a; WGAQOG 2000) results in a margin of exposure of 320 to 20 000. The margins of exposure for ocular effects are considered adequate to address uncertainties in the health effects and exposure data used to characterize risk.

Respiratory effects

An acute respiratory effect level of 2 ppm (2.8 mg/m^3) was identified on the basis of biologically significant increases in airway resistance observed in asthmatic volunteers exposed to hydrogen sulfide for 30 minutes in an exposure chamber (Jäppinen et al. 1990). Comparison of the respiratory effect level of 2 ppm with the upper-bounding ambient air concentration range of 0.001 ppm to 0.031 ppm (Alberta Environment 2000a; WGAQOG 2000) results in margins of exposure ranging from 60 to 2000.

The upper-bounding ambient air concentration of 0.031 ppm is the highest 99th percentile concentration obtained from a set of numerous 1-hour measurements taken near point sources across Canada over a span of several years, and this upper-bounding ambient air concentration encompasses the range of 99th percentile air levels for all point sources in the air monitoring database. This biologically significant increase in airway resistance in asthmatics in response to hydrogen sulfide exposure is not confounded by uncertainty associated with either variability between species or toxicokinetic differences between sexes. On the basis of these considerations, the margins of exposure derived—using a biologically relevant respiratory endpoint in human asthmatics (a susceptible subgroup)—are considered adequate to address uncertainties in the health effects and exposure data used to characterize risk for both healthy and susceptible asthmatic individuals.

For longer-term inhalation exposure risk characterization, the only endpoint available was an inhalation NOAEC of 10 ppm (14 mg/m^3), identified on the basis of nasal (portal of entry) olfactory neuronal loss observed in rats and mice exposed to 30 ppm (42 mg/m^3) or higher hydrogen sulfide for 10 weeks (Brenneman et al. 2000) or 90 days (Dorman et al. 2004). The comparison of this subchronic NOAEC of 10 ppm with the upper-bounding range of ambient air concentrations of 0.001 ppm to 0.031 ppm (Alberta Environment 2000b; WGAQOG 2000) results in margins of exposure ranging from 320 to 10 000. The margins of exposure for respiratory effects are considered adequate to address uncertainties in the health effects and exposure data used to characterize risk.

Neurological effects

Historically, neurotoxic effects have been documented in humans as a result of exposure to high levels of hydrogen sulfide via inhalation in occupational settings. Many case studies of acute human exposure to hydrogen sulfide reported neurological effects, including nausea, headaches, delirium, disturbed equilibrium, poor memory, neurobehavioural changes, olfactory paralysis, loss of consciousness or “knockdown,” tremors, and convulsions. Reports of concentrations causing these effects are limited, but it is estimated that levels in the range of 100 ppm to 200 ppm (140 mg/m^3 to 280 mg/m^3) can cause a loss of smell, and 500 ppm to 1000 ppm (700 mg/m^3 to 1400 mg/m^3) can cause loss of consciousness (US EPA 2003). Acute exposure to high levels (>500 ppm to 1000 ppm [>700 mg/m^3 to 1400 mg/m^3]) of hydrogen sulfide can be fatal. These levels, specific to industrial workplace settings, are several orders of magnitude higher than concentrations encountered in a community setting (0.0014 mg/m^3 to 0.0434 mg/m^3 or 0.001 ppm to 0.31 ppm); consequently, they are not considered relevant for general population risk characterization.

In a rat inhalation study in which whole-body exposures were 0, 10, 30, 80, or 400 ppm for 5 days, the NOAEC was 30 ppm and the LOAEC was 80 ppm (110 mg/m^3), as derived on the basis of significant reductions in spontaneous motor activity (ambulations and total movements; Struve et al. 2001). In addition, cognitive function, evaluated as learning and memory using a modified Morris water maze protocol, was not impaired following exposures (nose only) of up to 80 ppm hydrogen sulfide for 5 days. Following motor activity testing, Struve et al. (2001) analyzed the brains for catecholamines and found that there were no hydrogen sulfide-related decreases in brain catecholamine levels in the striatum, hindbrain, or hippocampus following exposures of up to 400 ppm. The authors concluded, on the basis of these data, that cognitive dysfunction is not anticipated to occur following short-term, repeated hydrogen sulfide exposures at the lowest tested concentration of 10 ppm (14 mg/m^3), a level identical to the US occupational limit (8-hour TLV) in effect since 2001.

Comparison of the cognitive function inhalation NOAEC of 30 ppm with the upper-bounding range of ambient air concentrations of 0.001 ppm to 0.031 ppm (Alberta Environment 2000b; WGAQOG 2000) results in margins of exposure ranging from 970 to 30 000. The margins of exposure for neurological effects are considered adequate to address uncertainties in the health effects and exposure data used to characterize risk.

Reproductive and developmental effects

No reproductive or developmental classifications by other national or international regulatory agencies were identified. The limited data identified in the literature did not show any evidence of reproductive or developmental effects associated with hydrogen sulfide in experimental animals. No reproductive or developmental effects, including neurodevelopmental effects, were observed in rats exposed to concentrations of up to 80 ppm (110 mg/m^3) in a study by Dorman et al. (2000). Neurodevelopmental effects, such as changes in Purkinje cell dendritic fields or neurotransmitter levels, were observed (Hannah and Roth 1991; Skrajny et al. 1992). However, no significant effects on behavioural performance or neuropathology were observed, and the evidence is considered insufficient to suggest adverse neurodevelopmental effects.

8.3.2 Incidental exposure

In addition to the ambient air concentrations derived from continuous monitoring, documented in publicly available reports, there is evidence of incidents during which members of the general population were potentially exposed to point-in-time, high concentrations or spikes of hydrogen sulfide in Canada on the basis of information received from provincial and municipal jurisdictions, mainly in Ontario.

Measured data from incidental releases of hydrogen sulfide around inactive oil and gas wells in southern Ontario have shown that wells can release levels of hydrogen sulfide that are sporadic or irregular, may persist for several hours, and can be emitted at levels greater than 100 ppm. The location of these wells may be on private property or in close proximity to neighbouring communities. Additionally, the reported values can be well in excess of the acute respiratory effect level of 2 ppm identified in this assessment as a critical effect level to characterize the risk from acute inhalation exposure.

Although these occurrences may be sporadic and acute in nature, single or repeated exposure to these higher levels of hydrogen sulfide may present a risk to human health. This is of particular significance in instances where hydrogen sulfide is emitted near residences as gas plumes may linger due to calm outdoor conditions and low wind speeds, which can result in limited turbulence and mixing of air (personal communication, email from the Ministry of Environment and Climate Change, Government of Ontario, to the Existing Substances Risk Assessment Bureau, Health Canada, dated April 4 2018; unreferenced).

8.3.3 Overall

Inhalation is expected to be the predominant route of general population exposure to hydrogen sulfide; thus, the health effects assessment was focused on data examining effects by this route. With respect to inhalation exposure to background ambient levels of hydrogen sulfide, which sodium bisulfide and sodium sulfide can contribute to, the margins between upper-bounding concentrations of hydrogen sulfide in ambient air and levels associated with critical health effects are considered adequate to address uncertainties in the health effects and exposure data used to characterize risk.

Reports of incidental exposure among the general population to hydrogen sulfide approach or exceed levels associated with adverse respiratory effects. Although it is recognized that there are limitations associated with the nature of the incidental exposure data, given the magnitude of reported incidental concentrations, the level at which acute health effects can occur, and the number of incidents that were reported, combined with the number of inactive oil and gas wells in Canada, it is considered appropriate to apply a precautionary approach when characterizing risk. Accordingly, there is a potential concern for human health associated with incidental exposure to hydrogen sulfide.

8.4 Uncertainties in evaluation of risk to human health

Given that hydrogen sulfide is a gas, the primary route of exposure examined is the inhalation route; other routes of exposure are of limited significance. The health effects database for hydrogen sulfide is also limited to the inhalation route. Long-term chronic experimental studies (that is, with exposures greater than 90 days) were not identified for hydrogen sulfide, sodium bisulfide, or sodium sulfide in this assessment, except for one limited oral study conducted with sodium sulfide.

Data on hydrogen sulfide releases for certain sectors (for example, metal and metal refining) located in proximity to human populations, were limited. However, confidence in the general population ambient air exposure assessment is high because a large set of ambient air level measurements, representative of most geographical locations in Canada, was available for several industries.

The availability of human data, particularly data complementing experimental observations in animal models, increases confidence in the evaluation. The studies used to determine the lowest concentrations at which either adverse effects or no adverse effects were obtained included both experimental animal and human studies, with the human studies indicating biologically relevant effects at inhalation concentrations lower than those reported in the animal studies. Using the human effect as the point of departure in the risk characterization (margins of exposure) increases confidence in the overall analysis.

Some limitations are associated with the data collected on incidental releases that may result in general population exposure to hydrogen sulfide.

As the data collected were observational in nature or were spot samples, typically taken in response to an incident or spill, they lack information that would generally be captured in a guideline-generated protocol study, such as a common limit of detection (LOD) and consistency between sampling sites (for example, distances from suspected leaks, sampling times, and exact locations). Additionally, the data reported may not reflect peak hydrogen sulfide concentrations as some are reported “above 100 ppm” (maximum level for some measurement devices) and as they are point-in-time measurements often measured some distance away from the suspected emission source of hydrogen sulfide. Therefore, while limitations within the data exist, they demonstrate the presence of incidental high levels of hydrogen sulfide in proximity to human populations, and the use of these data in this assessment is considered warranted on the basis of the level at which acute health effects can occur compared to the incidental high concentrations observed.

9. Consideration of subpopulations who may have greater susceptibility or greater exposure

There are groups of individuals within the Canadian population who, due to greater susceptibility or greater exposure, may be more vulnerable to experiencing adverse health effects from exposure to substances. Certain subpopulations are routinely considered throughout the assessment process, such as infants, children, and people of reproductive age. For example, developmental and reproductive toxicity studies are evaluated for potential adverse health effects. For the assessment of hydrogen sulfide, these subpopulations were taken into account. In addition, people living near inactive oil and gas wells who are more likely to be exposed to high levels of hydrogen sulfide from release events were considered. In this assessment, data was available to account for people who have asthma and who may be more susceptible to respiratory effects from exposure to hydrogen sulfide.

10. Conclusion

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

Considering all the information presented in this draft assessment, it is proposed that hydrogen sulfide (H_2S) meets the criteria under paragraph 64(*c*) of CEPA as it is entering or may enter the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health. It is further proposed to conclude that sodium bisulfide and sodium sulfide do not meet the criteria under paragraph 64(*c*) of CEPA as they are not entering or may not enter the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health.

It is therefore proposed to conclude that hydrogen sulfide meets one or more of the criteria set out in section 64 of CEPA, and sodium bisulfide and sodium sulfide do not meet any of the criteria set out in section 64 of CEPA. It is also proposed that hydrogen sulfide (H_2S) meets the persistence but not the bioaccumulation criteria as set out in the *Persistence and Bioaccumulation Regulations* of CEPA.

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Appendix A. Additional information on inactive oil and gas wells in Canada

In the upstream oil and gas industry, when a well becomes inactive (that is, it has not produced oil or gas, injected fluids, or disposed of waste for a period of time), the well may undergo suspension, abandonment, or reclamation—procedures designed to prepare the well for longer-term inactivity (AER 2019b; CAPP 2021). A well may also be designated as orphaned if there is no legally or financially responsible owner. These terms are further described below:

- **suspended**: A well that is temporarily not in production and which has been secured in accordance by applicable regulations or guidelines. A suspended well may continue production in the future or be abandoned by the well owner or operator.
- **abandoned**: A well that has been decommissioned (dismantled and plugged) by the owner, as prescribed by applicable regulations or guidelines. An abandoned well is permanently taken out of production.
- **reclaimed**: An abandoned well where the surrounding land has been returned to its original state (removal of equipment, surface reconstruction, etc.).
- **orphaned**: A well that has no owner—a legally or financially able party. A well can become orphaned at any stage of its life.

Table A 1. Inventory of oil and gas wells in Canada (values are rounded)below provides a summary of the number of inactive wells in various provinces and territories. Most of the inactive wells in Canada were identified in the western provinces of British Columbia, Alberta, and Saketchewan. A large number of inactive wells were also identified in Ontario, which has been attributed to the historic oil and gas activity in the province.

Table A 1. Inventory of oil and gas wells in Canada (values are rounded)

Province / territory	Active wells	Abandoned inactive wells	suspended inactive wells	orphaned inactive wells
British Columbia	9 900[a]	9 900[a]	4 500[a]	360[b]
Alberta[c]	156 000	82 000	90 000	7 700
Saskatchewan	34 400[d]	42 000[d]	25 000[d]	500[e]
Manitoba[f]	5 200	4 200	210	N/A[p]
Ontario[g]	3 000	9 500	650	900
Quebec[h]	N/A	775[*]	*	*
Newfoundland	N/A	25[i]	2[j]	N/A
New Brunswick[k]	N/A	800	N/A	N/A
Nova Scotia[l]	N/A	150	10	N/A
Prince Edward Island[m]	N/A	N/A	N/A	N/A
Northwest Territories[n]	N/A	600	85	N/A
Yukon[o]	N/A	60	15	N/A
Nunavut	N/A	N/A	N/A	N/A
Total	**208 500**	**150 010**	**120 472**	**9 460**

[*] In Quebec, inactive wells are not categorized as abandoned, suspended, or orphaned. Therefore, the number of gas and oil wells (775) represents all categories of inactive wells in the table.

[a] BCOGC 2020

[b] BCOGC 2021

[c] Alberta 2022

[d] Saskatchewan 2022a

[e] Saskatchewan. 2022b

[f] Manitoba. 2020

[g] OGSRL 2019.

[h] Ministère de l'Énergie et des Ressources naturelles du Québec 2021

i Newfoundland & Labrador Canada 2022

[j] Newfoundland & Labrador Canada 2019

[k] Note: The New Brunswick Borehole Database indicates that there are approximately 780 boreholes in New Brunswick, but only 300 are oil and oil & gas [accessed 2022 Apr].

[l] Nova Scotia 2012

[m] There are currently 20 exploratory wells on Prince Edward Island [accessed 2022 Apr].

[n] North West Territories 2021

[o] Yukon 2014

[p] Not available

Appendix B. Summary of health effects information for hydrogen sulfide

Table B 1. Experimental animals and *in vitro*

Endpoint	Lowest effect levels/results
Acute toxicity	Inhalation LC_{50} (rat) = 470 mg/m^3–820 mg/m^3 (Prior et al. 1988). Inhalation LC_{100} (rat) = 700 mg/m^3–2300 mg/m^3 (Beck et al. 1979; Lopez et al. 1989; Khan et al. 1990). Inhalation LC_{100} (mouse) = 1000 mg/m^3 (Smith and Gosselin 1964). Inhalation LC_{100} (rabbit) = 700 mg/m^3–1400 mg/m^3 (Kage et al. 1992). Respiratory effects Lowest LOEC: 10 ppm (14 mg/m^3) on the basis of a significant decrease in cytochrome oxidase activity in the liver of male Sprague-Dawley rats (6 per group) exposed to 0, 10, 30, 80, 200, or 400 ppm (0, 14, 42, 110, 280, or 560 mg/m^3) hydrogen sulfide for 3h. A significant decrease in oxidase activity in the liver was observed at 14 mg/m^3 and higher. A significant decrease in cytochrome oxidase activity in the lung was observed at 42 mg/m^3 and higher. A significant increase in sulfide concentration was observed at 110 mg/m^3 and higher in the lung and at 280 mg/m^3 and higher in the liver (Dorman et al. 2002). Other lowest LOEC: 10 ppm (14 mg/m^3) on the basis of a significant transient increase in the cellularity of nasal lavage fluid in male Fischer 344 rats (12 per group) exposed to 0, 10, 200, or 400 ppm (0, 14, 280, or 560 mg/m^3) hydrogen sulfide for 4 h. Per exposed group, 4 animals were sacrificed at 1, 20, and 44 h post-exposure. A significant increase in cellularity of nasal lavage fluid was observed at 14 mg/m^3 and higher. In the groups exposed to 14 mg/m^3 and 280 mg/m^3, changes were restored to original levels 20 h post-exposure. A significant increase in lactate dehydrogenase activity was observed at 280 mg/m^3 and higher, and a significant increase in alkaline phosphatase activity was observed at 560 mg/m^3 in bronchoalveolar lavage fluid. Changes in nasal lavage fluid may be an early marker in detecting mild lesions,

Endpoint	**Lowest effect levels/results**
	but histopathological evaluation is a more common practice (Lopez et al. 1987). Other LOEC: 615 mg/m^3 on the basis of transient histological changes in the lung and edematogenic effect in male Fischer 344 rats (12 per group) exposed to 0, 83, or 440 ppm (0, 116, or 615 mg/m^3) hydrogen sulfide for 4 h. Four animals per exposed group were sacrificed 1, 18, and 42 h post-exposure (Lopez et al. 1988a). <u>Neurological effects</u> Male Wistar rats (number of animals was not stated in secondary reference) were exposed to 100 ppm–500 ppm (139 mg/m^3–695 mg/m^3, values cited from US EPA 2003) hydrogen sulfide for 2 h. At 200 ppm (280 mg/m^3) and higher, a significant decrease in discriminated avoidance response was observed. At 300 ppm (417 mg/m^3) and higher, Sidman-type conditioned avoidance response was suppressed. Following exposure to 139 mg/m^3–280 mg/m^3 for 1 h, increased blood pressure and respiratory rates as well as histological and biochemical changes in respiratory tissues and fluid were observed (Higuchi and Fukamachi 1977). <u>Other studies</u> Elovaara et al. 1978; Rogers and Ferin 1981; Kombian et al. 1988; Lopez et al. 1988b; Khan et al. 1990, 1991; Prior et al. 1990; Green et al. 1991; Kohno et al. 1991; Lefebvre et al. 1991; Brenneman et al. 2002.
Short-term toxicity	<u>Respiratory effects</u> Lowest LOEC: 10 ppm (14 mg/m^3) on the basis of a significant decrease in cytochrome oxidase activity in lung mitochondria in male Fischer 344 rats (number of animals used was not stated) exposed to 0, 1, 10, or 100 ppm (0, 1.4, 14, or 140 mg/m^3) hydrogen sulfide 8 h/day, 5 days/week, for 5 weeks. No effect on the enzymes in liver mitochondria was observed. A non-significant decreasing trend in the brain mitochondria for cytochrome oxidase activity was observed. In erythrocytes, a significant decrease in superoxide dismutase activity was observed at 140 mg/m^3. No histopathological examinations were performed (Khan et al. 1998).

Endpoint	Lowest effect levels/results
	<u>Neurological effects</u> Lowest NOAEC: 30 ppm (42 mg/m^3) and LOAEC: 80 ppm (110 mg/m^3) on the basis of a significant reduction in motor activity and body temperature in male CD rats exposed to nose-only inhalation of hydrogen sulfide at 0, 30, 80, 200, or 400 ppm (0, 42, 110, 280, or 560 mg/m^3) for 3 h/day for 5 consecutive days. One group of rats (10 per exposed group) was tested daily for spatial learning with a Morris water maze, immediately after exposure. Another group of animals (10 per exposed group) was tested for spontaneous motor activity after the fifth exposure. Significant reductions in motor activity were observed at 80 ppm (110 mg/m^3) and higher. In the Morris water maze testing, animals exposed to 400 ppm had significantly increased latencies in both the acquisition phase (days 1–4) and the probe trial (day 5) compared to control animals. No effects on catecholamine levels in the striatum, hindbrain, or hippocampus from the animals tested for motor activity were observed (Struve et al. 2001). Male CD rats (5–7 per group) were exposed to hydrogen sulfide by whole-body inhalation at 0, 10, 30, or 80 ppm (0, 14, 42, or 110 mg/m^3) for 3 h/day for 5 consecutive days. Multiple fixed-interval schedule operant performance was assessed daily and compared with the week pre-exposure and the week post-exposure. No significant effect on fixed-interval schedule performance was observed. Learning and memory were not impaired by hydrogen sulfide exposure of up to 80 ppm on the basis of the findings of the Morris water maze testing. Motor activity was not affected by hydrogen sulfide exposure (Struve et al. 2001). Other LOAEC: 125 ppm (174 mg/m^3) on the basis of mild impaired performance during reacquisition of a reversed contingency radial arm maze task in male Sprague-Dawley rats (10–12 per group) exposed to 0 or 125 ppm (0 or 174 mg/m^3) hydrogen sulfide 4 h/day, 5 days/week, for 5 weeks. No effects on memory retention or acquisition were observed (Partlo et al. 2001).

Endpoint	Lowest effect levels/results
	Other studies Kośmider et al. 1967; Curtis et al. 1975; Haider et al. 1980; Skrajny et al. 1996; Brenneman et al. 2002; Dorman et al. 2002.
Subchronic toxicity	Respiratory effects Lowest NOAEC: 10 ppm (14 mg/m^3) and LOAEC: 30 ppm (42 mg/m^3) on the basis of mild to moderate olfactory neuron loss and basal cell hyperplasia in the olfactory mucosa in male Sprague-Dawley rats (12 per group) exposed to 0, 10, 30, or 80 ppm (0, 14, 42, or 110 mg/m^3) hydrogen sulfide for 6 h/day, 7 days/week, for 10 weeks. Only the nasal cavity and the olfactory system were examined. No effects were observed in the control animals or in animals exposed to 10 ppm (14 mg/m^3) hydrogen sulfide (Brenneman et al. 2000). Other lowest NOAEC: 10 ppm (14 mg/m^3) and LOAEC: 30 ppm (42 mg/m^3) on the basis of a significant increase in olfactory neuron loss in male and female Fischer 344 rats and B6C3F1 mice and in female Sprague-Dawley rats. A significant olfactory neuron loss was observed at 80 ppm (110 mg/m^3) in male Sprague-Dawley rats. A 100% incidence of rhinitis was observed in B6C3F1 mice at 110 mg/m^3 (Dorman et al. 2004). Dorman et al. (2004) is a reassessment of the nasal and lung histopathology from CIIT (1983a,b,c) as described below. Other LOEC: 80 ppm (110 mg/m^3) in Fischer 344 rats, Sprague-Dawley rats, and B6C3F1 mice exposed to 0, 10.1, 30.5, or 80 ppm (0, 14, 42, or 112 mg/m^3) hydrogen sulfide for 6 h/day, 5 days/week, for 90 days (CIIT 1983a,b,c). In Sprague-Dawley rats (10 of each sex per group), the LOEC of 110 mg/m^3 was based on a decrease of body weight in females and a decrease of absolute brain weight in males. At 110 mg/m^3, feed consumption and body weights were reduced in both sexes. No significant differences in hematology, serum chemistry, urinalysis, ophthalmology, neuropathology, or histopathology were observed (CIIT 1983c). In Fischer 344 rats (10 of each sex per group), the LOEC of 110 mg/m^3 was based on a decrease in feed

Endpoint	Lowest effect levels/results
	consumption and body weight in both sexes and an increase in relative brain weight in males. A significant elevated sulfhemoglobin level was observed in males at 110 mg/m^3. No significant differences in hematology, serum chemistry, urinalysis, ophthalmology, neuropathology, or histopathology were observed (CIIT 1983b). In B6C3F1 mice (10 of each sex per group), the LOEC of 110 mg/m^3 was based on reduced feed consumption and body weight and inflammation of the nasal mucosa in both sexes. Significant decrease of absolute but not relative heart, liver, and spleen weights in males and a significant decrease in kidney weight in females were observed at 110 mg/m^3. No compound-related gross lesions or significant differences in hematology, serum chemistry, urinalysis, ophthalmology, or neuropathology were observed (CIIT 1983a). <u>Other studies</u> Wetterau et al. 1964; Anderson 1987; Dorman et al. 2002; Moulin et al. 2002.
Chronic toxicity/carcinogenicity	No studies were identified.
Reproductive/developmental toxicity	Reproductive and developmental NOEC = 80 ppm (110 mg/m^3). Sprague-Dawley rats (12 of each sex per group) were exposed to 0, 10, 30, or 80 ppm (0, 14, 42, or 110 mg/m^3) hydrogen sulfide for 6 h/day, 7 days/week, for 2 weeks prior to mating and during the 2-week mating period. For pregnant females, exposure continued from gestational day (GD) 0 to GD 19. The dams and their pups were exposed from postnatal day (PND) 5 to PND 18. For males, exposure continued for 70 days. In terms of reproductive effects, no statistically significant effects on reproductive performance, mating index, fertility index, post-implantation loss per litter, number of late resorptions, or stillbirths were observed. No effects upon the number of live pups, litter size, average length of gestation, or average number of implants were observed. Testicular tubular degeneration was 42% in males exposed to 112 mg/m^3 compared with 17% in control males, which was not statistically significant. Relative ovary weights were

Endpoint	**Lowest effect levels/results**
	significantly decreased in low-exposure group females only. In terms of developmental effects, no significant differences were observed in pup weight gain or development, behavioural performance, or neuropathology. Behavioural assessment included motor activity (PNDs 13, 17, 21, 60 ± 2), passive avoidance (PNDs 22 ± 1, 62 ± 3), functional observational battery (PND 60 ± 2), acoustic startle response (PNDs 21, 62 ± 3), and neuropathology (PNDs 23 ± 2, 61 ± 2). Systemic toxicity with a LOEC of 10 ppm (14 mg/m^3) was observed in the F_0 parents on the basis of decreased relative and absolute adrenal weights in males and decreased relative ovary weights in females (Dorman et al. 2000). Other studies: Andrew et al. 1980; Saillenfait et al. 1989; Hayden et al. 1990a,b.
Neurodevelopmental effects	Lowest LOEC = 20 ppm (28 mg/m^3) was based on significant alterations in the architecture and growth characteristics of the Purkinje cell dendritic fields in pups when pregnant Sprague-Dawley rats (10 per group) were exposed to 0, 20, or 50 ppm (0, 28, or 70 mg/m^3) hydrogen sulfide for 7 h/day from GD 5 to PND 21. Only developing cerebellar Purkinje cells were examined (one Purkinje cell from each pup). In pups exposed to 28 or 70 mg/m^3, segment length was significantly increased over the low and middle branching orders, and the mean vertex path length was also significantly increased in the Purkinje cells. The authors concluded that these effects were indicative of significant alterations in the architecture and growth characteristics of the Purkinje cell dendritic fields (Hannah and Roth 1991). The US EPA (2003) questioned whether these alterations could be seen as adverse, as “the effects reported are highly selective and could be due to environmental factors not directly related to exposure including variability resulting from the restricted sampling technique (that is, one Purkinje cell per pup).” Other lowest LOEC = 20 ppm (28 mg/m^3) was based on a significant increase in serotonin levels in the frontal cortex of exposed pups when 20 pregnant

Endpoint	Lowest effect levels/results
	Sprague-Dawley rats were exposed to 0, 20, or 75 ppm (0, 28, or 105 mg/m^3) hydrogen sulfide for 7 h/day from GD 5 to PND 21. At 28 mg/m^3, a significant increase in serotonin levels in the frontal cortex on PND 21 was observed. At 105 mg/m^3, a significant increase in serotonin levels was observed in the cerebellum and frontal cortex on PNDs 14 and 21. At 105 mg/m^3, a significant increase in norepinephrine levels in the cerebellum was observed on PNDs 7, 14, and 21. At 28 mg/m^3, a significant decrease in norepinephrine levels was observed in the frontal cortex on PNDs 14 and 21 (Skrajny et al. 1992). Other studies: Hannah et al. 1989, 1990; Roth et al. 1995.
Genotoxicity and related endpoints	*In vitro* Mutagenicity: Negative: Ames tests, *Salmonella typhimurium* TA97, TA98, TA100 in the presence or absence of metabolic activation S9 at dose levels of 0, 17, 57, 175, 582, or 1750 µg/plate (Hughes et al. 1984). Comet assays [using sodium sulfide (Na_2S) as hydrogen sulfide is released when Na_2S is dissolved in aqueous solution]: Positive: Nontransformed human small intestine FHs 74 Int cells were treated with concentrations of $Na_2S \cdot 9H_2O$ ranging from 250 µM to 2000 µM for 2 hours. Dose-dependent responses were observed. Cytotoxicity was not observed (Attene-Ramos et al. 2010). Negative: Chinese hamster ovary (CHO) cells were treated with Na_2S for 4 hours at concentrations ranging from 25 µM to 5000 µM. Acute cytotoxicity was observed at ≥7500 µM (Attene-Ramos et al. 2006). Positive: In a modified comet assay, DNA repair was inhibited using hydroxyurea and 1-β-D-arabinofuranosylcytosine (AraC). CHO cells were treated with Na_2S for 2 hours at concentrations ranging from 250 µM to 3000 µM (Attene-Ramos et al. 2006).

Endpoint	Lowest effect levels/results
	Negative: A Cl.16E subclone of the human colonic cancer cells HT29 was treated with Na_2S at a concentration of 2000 µM (Attene-Ramos et al. 2006). Positive: In a modified comet assay, DNA repair was inhibited using hydroxyurea and 1-β-D-arabinofuranosylcytosine (AraC). A Cl.16E subclone of the human colonic cancer cells HT29 was treated with Na_2S at concentrations ranging from 500 to 2000 µM (Attene-Ramos et al. 2006). No other studies were identified.

Table B 2. Human studies

Endpoint	Lowest effect levels/results
Ocular effects	WHO (2000) reported a threshold for eye irritation at 10 ppm–20 ppm (15 mg/m^3–30 mg/m^3) and serious eye damage at 50 ppm–100 ppm (70 mg/m^3–140 mg/m^3) on the basis of the findings presented in the Savolainen study (1982). Detailed information was not reported in WHO (2000). In a community near a paper mill with an environmental exposure to an annual mean concentration of 6 µg/m^3 of hydrogen sulfide (daily peaks of hydrogen sulfide concentrations as high as 100 µg/m^3) and co-exposure to methyl mercaptan and methyl sulfides, eye irritation was reported 12 times more frequently than in communities without exposure (Jaakkola et al. 1990). A group of viscose rayon workers (123 males) exposed to hydrogen sulfide and/or carbon disulfide for at least a year and a group of 67 referents were given self-administered questionnaires with questions concerning eye complaints. For the viscose rayon workers, personal exposure levels for hydrogen sulfide and carbon disulfide were measured and varied from 0.2 mg/m^3–8.9 mg/m^3 and 4 mg/m^3–112 mg/m^3, respectively. The referents were not exposed to hydrogen sulfide, carbon disulfide, or any other irritant substances occupationally. After adjusting for age and smoking, viscose rayon workers exposed to >5 mg/m^3 hydrogen sulfide had significantly more eye complaints than the referents (Vanhoorne et al. 1995).

Endpoint	Lowest effect levels/results
	Other studies: Riffat et al. 1999.
Respiratory effects	Lowest LOEC: 0.5 ppm (0.7 mg/m^3) was based on a significant decrease in RER in the "low fit" males exercising at maximum level. A total of 16 healthy male volunteers and 5 healthy female volunteers were exposed to 0, 0.5, 2, or 5 ppm (0, 0.7, 2.8, and 7 mg/m^3) hydrogen sulfide via oral inhalation during graded exercise until exhaustion. Exercise duration ranged from 13 min to 16 min. The male subjects were ranked in serial order on the basis of their relative maximum oxygen uptake (VO$_2$ max) and classified into "high fit" (mean age 24 ± 5.1 SD) and "low fit" (mean age 26.3 ± 5.9 SD) groups, whereas females (mean age 23.8 ± 4.7 SD) were not classified. The mean VO$_2$ max values for "high fit" and "low fit" groups were 46.9 ± 3.9 SD ml/kg per minute and 36.9 ± 3.2 SD ml/kg per minute, respectively. A number of physiological and pulmonary parameters were measured at two submaximal and maximal exercise levels. In the "high fit" group, exposure at 5 ppm resulted in a significant increase in absolute oxygen consumption and blood lactate concentration and a significant reduction in RER during submaximal and maximal exercise. In the "low fit" group, a significant decrease in RER was observed at 0.5, 2, and 5 ppm at the maximal exercise level and at 2 and 5 ppm at the submaximal exercise level. At 5 ppm, a significant increase in blood lactate concentration was observed during all exercise levels, and a significant increase in absolute oxygen consumption was observed at the maximal exercise level. In the female group, significant increases in absolute oxygen consumption and relative oxygen consumption were observed at 5 ppm during maximal exercise. RER was significantly decreased at 5 ppm during all exercise levels (Bhambhani and Singh 1985). Other effect level: 2 ppm (2.8 mg/m^3) in 10 asthmatic volunteers (7 women with mean age 44.1 [ranging from 31 to 61] and 3 men with mean age 40.7 [ranging from 33 to 50]) exposed to 2.8 mg/m^3 hydrogen sulfide for 30 min in an exposure chamber. The subjects had had bronchial asthma for 1 to 13 years (mean 3.7 years) and had been taking medications. However, they did not take medications for 2 days prior to the study. Severe asthmatics were not included in the study. On average, airway resistance increased by 26.3%, and specific airway conductance (SGaw) decreased by 8.4%These effects were not statistically significant. The SGaw decreased in 6 subjects and

Endpoint	Lowest effect levels/results
	increased in 4 subjects. In 2 of the 4 subjects with decreased SGaw, changes were greater than 30% for both airway resistance and SGaw, indicating possible bronchial obstruction in the 2 subjects. Of the 10 subjects, 3 reported headaches after exposure. No significant differences in forced vital capacity, forced expiratory volume in 1 s, orforced expiratory flow were observed. It should be noted that the investigators compared pre- and post-exposure results only and did not expose subjects to both treatment and control conditions, nor were non-asthmatic control subjects used for comparison. The authors also examined possible respiratory effects associated with hydrogen sulfide in 26 male pulp mill workers (mean age 40.3, range 22 to 60 years old). Among the 26 workers, 6 were smokers, 4 had previous allergies, and 5 were atopic subjects. These workers were exposed to hydrogen sulfide in the workplace with exposure levels ranging from 1 ppm to 11 ppm. Respiratory effects were compared on the basis of responses to standard histamine challenges performed after a holiday or one day away from work, with responses obtained at the end of the work day. No statistically significant changes in respiratory function (forced vital capacity [FVC], forced expiratory volume in 1 s [FEV_1], and bronchial responsiveness) were observed (Jäppinen et al. 1990). Other LOEC: 2 ppm (2.8 mg/m^3) was based on significantly reduced RER in healthy male volunteers (16 in total, mean age 25.2 ± 5.5 SD) exposed to 0, 0.5, 2, or 5 ppm (0, 0.7, 2.8, or 7 mg/m^3) hydrogen sulfide via oral inhalation during graded cycle exercise until exhaustion. Exposure duration was at least 16 min. Physiological parameters were measured at three levels, two submaximal and maximal levels. RER was significantly reduced at both 2 and 5 ppm during maximal exercise and at 5 ppm during submaximal exercise. Maximum oxygen uptake (VO_2 max) was significantly increased during maximal exercise at 5 ppm. A significant increase in blood lactate levels was observed at all exercise levels in subjects exposed to 5 ppm hydrogen sulfide. Heart rate, expired ventilation, and maximal power output were not affected (Bhambhani and Singh 1991). A group of healthy subjects (13 men with mean age 24.7 ± 4.6 SD, 12 women with mean age 22.0 ± 2.1 SD) was exposed to 0 or 5 ppm (7 mg/m^3) hydrogen sulfide for 30 min via oral inhalation during exercise at 50% of their predetermined maximal aerobic power. No significant effects were observed on

Endpoint	Lowest effect levels/results
	physiological, perceptual, or arterial blood parameters. Biochemical properties of skeletal muscle were analyzed immediately following exercise. Muscle lactate, lactate dehydrogenase, and cytochrome oxidase were non-significantly decreased. In men, citrate synthase was significantly decreased at 5 ppm, which the authors suggested might be an indication of aerobic metabolism inhibition (Bhambhani et al. 1994, 1996b). A group of healthy subjects (9 men with mean age 24.7 ± 6.4 SD, 10 women with mean age 21.8 ± 3.0 SD) was exposed to 0 or 10 ppm (14 mg/m^3) hydrogen sulfide for 15 min via oral inhalation during exercise at 50% of their predetermined maximal aerobic power. No significant effects on pulmonary function were observed with variables derived from the flow volume loop, maximum ventilation volume, and diffusion capacity of the lung for carbon monoxide (Bhambhani et al. 1996a). A group of healthy subjects (15 men with mean age 23.4 ± 5.2 SD, 13 women with mean age 21.8 ± 3.0 SD) was exposed to 0 or 10 ppm (14 mg/m^3) hydrogen sulfide for 30 min via oral inhalation during exercise at 50% of their predetermined maximal aerobic power. A significant decrease in oxygen uptake and a significant increase in both the RER and blood lactate levels were observed in both men and women at 10 ppm. A non-statistically significant increase in muscle lactate levels and a non-statistically significant decrease in muscle citrate synthase activity were observed (Bhambhani et al. 1997). Other studies: Higashi et al. 1983; Jäppinen et al. 1990; Richardson 1995; Hessel et al. 1997; Buick et al. 2000; Campagna et al. 2004.
Neurological effects	A group of 74 healthy subjects (35 females and 39 males, mean age = 24.7 ± 4.2 SD; mean years of education = 16.5 ± 2.4 SD) was exposed to 0.05, 0.5, and 5 ppm (0.07, 0.7, and 7 mg/m^3) hydrogen sulfide in a random order for 2 hours over 3 weeks in an exposure chamber. It should be noted that effects were compared before and after exposure for each subject and that a non-exposed control group was not included in the study. Odour ratings, sensory function (postural sway, visual acuity, and visual contrast sensitivity) and cognitive tests (simple reaction time and continuous performance tests, finger tapping test, symbol-digit substitution test, auditory verbal learning test) were examined. Significant effects were observed for odour detection,

Endpoint	Lowest effect levels/results
	irritation, and anxiety following hydrogen sulfide exposure over time at all exposure levels. A significant decline in cognitive recall through auditory verbal learning was observed at all exposure levels. As no significant effects on other sensory or cognitive measures were observed, the authors suggested that the decline in verbal learning could be due to fatigue (Fiedler et al. 2008). In a cohort study, 103 subjects were exposed to various durations of low-level environmental exposure of hydrogen sulfide between 1 and 22 years prior to the assessment. In some cases, exposure levels were not reported; in others, they were estimated on the basis of various measured levels. Some subjects were concurrently exposed to other substances. A number of neurobehavioural deficits were identified in the subjects, including alterations in balance, visual fields, choice reaction time, colour discrimination, grip strength, and delayed verbal recall (Kilburn 1997, 1999). In another cohort study, neurobehavioural assessment was conducted in 19 subjects who had been environmentally exposed to hydrogen sulfide for periods ranging from 20 min to 9 years (exposure levels were not quantified). The assessment occurred 1.7 to 22 years after exposure, and none of the subjects had lost consciousnessfrom exposure. A referent population was used for comparison. Exposed subjects exhibited deficits in reaction time, balance, blink reflex, colour error scores, visual performance, grip strength, hearing, and a number of cognitive parameters (Kilburn 2003). Other studies: Kilburn and Warshaw 1995; Hirsch 2002; Inserra 2004; Farahat and Kishk 2010.
Case studies	A number of case studies of hydrogen sulfide exposure were reported in which concentrations and durations of exposure were usually unquantified and co-exposure to other chemicals was frequent. Some of the effects reported included loss of consciousness; death; pulmonary, intracranial, and cerebral edema; hemorrhagic bronchitis; chest pain; respiratory distress; bradycardia; cardiac arrhythmias and irregularities; increase in blood pressure; cyanosis; nausea; vomiting; headache; dyspnea; eye irritation and other ocular effects such as visual impairment, photophobia and corneal erosion; nasal irritation; reduced hearing; hemoptysis; and neurological effects such as coma, seizures, dizziness, dementia, decreased ability to

Endpoint	**Lowest effect levels/results**
	communicate, decreased attention and concentration, memory impairment, impaired visual perception and coordination, impaired motor function, ataxia, cerebral atrophy, and irritability (Allyn 1931; Ahlborg 1951; McDonald and McIntosh 1951; Spolyar 1951; Breysse 1961; Milby 1962; Krekel 1964; Adelson and Sunshine 1966; Thoman 1969; Simson and Simpson 1971; Burnett et al. 1977; Osbern and Crapo 1981; Hagley and South 1983; Beauchamp et al. 1984; Arnold et al. 1985; Audeau et al. 1985; Deng and Chang 1987; Luck and Kaye 1989; Wasch et al. 1989; NIOSH 1991; Parra et al. 1991; Tvedt et al. 1991a,b; Kilburn 1993; Snyder et al. 1995; Hall and Rumack 1997; Watt et al. 1997; Fenga et al. 2002; Kage et al. 2002, 2004; Nelson and Robinson 2002; CSB 2003; Hendrickson et al. 2004; Nam et al. 2004; Nikkanen and Burns 2004; Smith and Cummins 2004; Miyazato et al. 2013; Sastre et al. 2013).
Reproductive and developmental effects	In a retrospective study of 2853 female petrochemical workers in China (from oil refinery, chemical, polyester, resin, carpet, and non-chemical plants), 1620 women reported exposure to petrochemicals. A significantly increased risk of spontaneous abortions was identified in workers with frequent petrochemical exposures (OR = 2.7, 95% CI = 1.8–3.9). The possible confounders of age, education level, plant, shift of work, standing and kneeling at work, noise level, dust level, passive smoking, and diets were adjusted for. When the risk associated with hydrogen sulfide exposure was examined, the OR was 2.3 with 95% CI = 1.2–4.4. In addition, elevated ORs were observed for benzene (OR = 2.5 with 95% CI = 1.7–3.7) and gasoline (OR = 1.8 with 95% CI = 1.1–2.9). However, no exposure information regarding the first trimester was available. Odds ratios for other effects were not investigated (Xu et al. 1998). <u>Neurodevelopmental effects</u> In a case study, a 20-month-old child was exposed to at least 0.6 ppm (0.84 mg/m^3) hydrogen sulfide and other unspecified chemicals emitted from a coal mine for nearly 1 year. The child was admitted to the hospital with ataxia, choreoathetosis, dystonia, and inability to stand, where a brain scan suggested toxic encephalopathy. Shortly after admission, the child recovered spontaneously. After 10 weeks of admission, ataxia had resolved, and choreoathetoid movements were reduced. The repeat brain scan was normal (Gaitonde et al. 1987).

Endpoint	**Lowest effect levels/results**
Epidemiological study	A number of ecological epidemiological, community-based, and sulfate mill studies were available. Exposure levels were usually unquantified, and co-exposure to a number of other chemicals was common. In most cases, inadequate data were available to draw conclusions of possible correlations between hydrogen sulfide exposure and health effects. Some of the health effects assessed included mortality, cataracts, conjunctiva disorders, orbit disorders, nervous system disorders, sense organ disorders, respiratory system-related disorders, and cancers (Burnett et al. 1977; Hemminki and Niemi 1982; Arnold et al. 1985; Schechter et al. 1989; Jaakkola et al. 1990; Jäppinen and Tola 1990; Haahtela et al. 1992; Marttila et al. 1994a,b, 1995; Kilburn and Warshaw 1995; Partti-Pellinen et al. 1996; Bates et al. 1997, 1998, 2002; Legator et al. 2001; Lewis et al. 2003; Thorn and Beiger 2004).

Appendix C. Summary of hydrogen sulfide ambient air concentration data

Table C 1. Hydrogen sulfide concentrations near pulp and paper industry

Sampling location/year (s)	Sampling regime	Average*	99th percentile**	Maximum***	Reference
Nova Scotia, New Brunswick, British Columbia, Quebec 1989–1998	Air sampled continuously for various durations at 64 sites (~21 000 samples per site)	2.7 ppb (3.78 µg/m^3) New Brunswick between Jan 1989 and Jul 1994	31 ppb (43.4 µg/m^3) Nova Scotia site, between 1994 and 1998	503 ppb (714 µg/m^3) Nova Scotia site, between 1994 and 1998	WGAQOG 2000

Sampling location/year (s)	Sampling regime	Average*	99th percentile**	Maximum***	Reference
Nova Scotia, Newfoundland, New Brunswick, Ontario, Manitoba, Saskatchewan, British Columbia, Quebec$^+$ 1999–2003	Air sampled continuously every hour (for various durations ranging from 2 to 5 years) at 50 mills	1.7 ppb (2 µg/m^3) Fort Frances, ON, 450 m from mill	18.6 ppb (26.8 µg/m^3) Red Rock, ON, located 480 m from mill, over year 2001	23.4 ppb (33.7µg/m^3) Fort Frances ON, over year 2001	Environment Canada 2004b
Quebec (Cap-de-la-Madeleine) 1979–1994	Air sampled continuously every hour for the length of the sampling period at 1 location	NA	NA	0.5 ppb (0.7 µg/m^3)	MEQ 1997

* Typically, an average of all hourly samples over the sampling period is calculated for each station in the study or database; the highest average amongst stations is provided here.

** 99th percentiles of hourly samples over the sampling period are calculated for each monitoring station in the study; the highest 99th percentile is provided here.

*** Represents the highest 1-hr concentration amongst all 1-hr samples measured in the study.

$^+$ Based on TRS measurements; H_2S concentration calculated based on the assumption that TRS contains up to 60% H_2S.

Table C 2. Hydrogen sulfide concentrations near oil and gas operations

Sampling location/year(s)	Sampling regime	Average*	99th percentile **	Maximum***	Reference
Alberta May 2007–May 2017	Air sampled continuously every hour at 35 stations	0.97 ppb (1.35 µg/m^3)	15 ppb (20.9 µg/m^3) Bonnyville Station	113 ppb (162 µg/m^3) Scotford Station No. 2 on October 15, 2015, 9 am	CASA 2017

Sampling location/year(s)	**Sampling regime**	**Average***	**99th percentile ** **	**Maximum*****	**Reference**
Alberta May 2007–May 2012	Air sampled continuously every hour at 35 stations	1.4 ppb (1.95 µg/m^3)	21 ppb (29.3 µg/m^3) Mildred Lake, Alberta	100 ppb (140 µg/m^3) Reported at Mildred Lake station on October 25, 2009, 8 pm	CASA 2017
Alberta May 2012–May 2017	Air sampled continuously every hour at 35 stations	1.0 ppb (1.39 µg/m^3)	17 ppb (23.7 µg/m^3) Reported from Scotford Station No. 2	113 ppb (158 µg/m^3) Reported from Scotford Station No. 2 on October 15, 2015, 9 am	CASA 2017
May 2017–April 2019	Air sampled continuously every hour at 35 stations	0.63 ppb (0.88 µg/m^3)	7.17 ppb (10 µg/m^3)	36 ppb (50.2 µg/m^3)	CASA 2019
Alberta (Wood Buffalo regional air shed) 2017–2018	Air sampled continuously every hour at 13 stations	0.1ppb – 0.6 ppb (0.14 µg/m^3 –0.86 µg/m^3)	0.4–6.5 ppb (0.57 µg/m^3 –9.36 µg/m^3)	3.5 ppb – 32.8 ppb (5.04 µg/m^3 – 47.27 µg/m^3)	WBEA 2018
Alberta (Wood Buffalo regional air shed) 2015	Continuous 1-hr sampling at 8 sites	0.7 ppb (0.98 µg/m^3) Annual average	NA	36 ppb (50.4 µg/m^3) Max 24-hr average: 6 ppb (8.4 µg/m^3) across all sites	WBEA 2016
Quebec (Montreal) 1979–1994	Air sampled continuously every hour at 1 location	NA	NA	0.3 ppb –0.5 ppb (0.42 µg/m^3 – 0.7 µg/m^3)	MEQ 1997

Sampling location/year(s)	**Sampling regime**	**Average***	**99th percentile ** **	**Maximum*****	**Reference**
Alberta, Saskatchewan, northern British Columbia April 2001–January 2003	Air sampled continuously every hour for 3 years at 1100 sites	0.2 ppb (0.28 µg/m^3)	0.53 ppb (0.74 µg/m^3) 95th percentile across all samples at all sites	NA	WISSA 2006
Saskatchewan January 1–December 31, 2018	Continuous	0.6 ppb – 0.9 ppb (0.86 µg/m^3 –1.29 µg/m^3) Annual average		1-hr 18.5 ppb (26.6 µg/m^3) 24-hr 3.7 ppb (5.3 µg/m^3)	GPAZ 2018
Saskatchewan 2017	Continuous	0.5 ppb –1.0 ppb (0.72 µg/m^3 – 1.4 µg/m^3) Annual average	NA	95.7 ppb 1-hr 13.4 ppb 24-hr	SESAA 2018
Saskatchewan (Regina) 2002–2006	Continuous hourly sampling at 2 sites	NA	NA	<10.8 ppb – 30.2 ppb (<15.1–42.3 µg/m^3)	Golder Associates 2007
Northwest Territories 2008–2009	2 sites	0.027 ppb – 19.1 ppb (0.04 µg/m^3 – 27.5 µg/m^3) Hourly measurements averaged over a month	NA	58 ppb (4.2–81.2 µg/m^3)	Chepelkevitch 2009

Sampling location/year(s)	**Sampling regime**	**Average***	**99th percentile ****	**Maximum*****	**Reference**
Northwest Territories 2014	Continuous 1-hr sampling at 1 station (Norman Wells)	NA	NA	2.0 ppb (2.8 µg/m^3) Max 24-hr average: 1.8 ppb (2.52 µg/m^3)	NWT 2014
Northwest Territories 2012	Continuous 1-hr sampling at 1 station (Inuvik, Fort Liard, Norman Wells)	NA	NA	2 ppb (2.8 µg/m^3)	NWT 2012
Northwest Territories 2010	Continuous 1-hr sampling at 1 station (Inuvik, Fort Liard, Norman Wells)	1-hr average 2.77 ppb (4 µg/m$^{3)}$	NA	24-hr average 2.77 ppb (4 µg/m^3)	NWT 2010
Northwest Territories 2006–2007	Passive monitoring at 2 stations	3.5 ppb – 19.2 ppb (5.0 µg/m^3 – 27.6 µg/m^3) 24-hr average	NA	NA	Girard 2007
Nova Scotia, New Brunswick, British Columbia, Quebec 1989–1998	Air sampled continuously every hour for various durations at 18 sites	1.37 ppb (2 µg/m^3) BC site, over 5 years (1994–1998)	12ppb (16.6 µg/m^3) Manitoba site, between May 1999–January 2000	113 ppb (157 ug/m^3) Quebec site, 1990–1998	WGAQOG 2000

Sampling location/year(s)	Sampling regime	Average*	99th percentile **	Maximum***	Reference
New Brunswick (Apohaqui, near Sussex) October 2012–April 2013	Continuous sampling every 5 minutes	0.2 ppb TRS (0.12 ppb hydrogen sulfide) 1-hr average	NR	0.36 ppb TRS (0.216 ppb hydrogen sulfide)	Health Canada 2014
New Brunswick (Apohaqui, near Sussex) October 2012–October 2013	Continuous sampling every 5 minutes	0.2 ppb TRS (0.12 ppb hydrogen sulfide) 1-hr average	NR	1.9 ppb TRS (1.14 ppb hydrogen sulfide)	Health Canada 2015
New Brunswick (Penobsquis, near Sussex) June 2014 – March 2015	Continuous sampling every 5 minutes	0.1 ppb TRS (0.06 ppb hydrogen sulfide)	NR	1.1 ppb TRS (0.66)	Health Canada 2017
New Brunswick (Penobsquis, near Sussex) June 2014–November 2014	Continuous sampling every 5 minutes	0.1 ppb TRS (0.06 ppb hydrogen sulfide)	NR	0.8 ppb TRS (0.48 ppb hydrogen sulfide)	Health Canada 2017

*Typically, an average of all hourly samples over the sampling period is calculated for each station in the study or database; the highest average amongst stations is provided here.

** 99th percentiles of hourly samples over the sampling period are calculated for each monitoring station in the study/database; the highest 99th percentile is provided here.

*** Represents the highest 1-hr concentration amongst all 1-hr samples measured in the study.

NR: not reported

Table C 3. Hydrogen sulfide concentrations near wastewater treatment systems

Sampling location/year(s)	Sampling regime	Average*	99th percentile**	Maximum***	Reference
Alberta (Bonnybrook/ Calgary) 1989–2003	Air sampled continuously every hour at 1 location	1.2 ppb (1.7 µg/m^3)	NA	38 ppb (53 µg/m^3) Max 24-hr average: 7.2 ppb (10 µg/m^3)	Hoeksema 2004

* Typically, an average of all hourly samples over the sampling period is calculated for each station in the study or database; the highest average amongst stations is provided here.

** 99th percentiles of hourly samples over the sampling period are calculated for each monitoring station in the study; the highest 99th percentile is provided here.

*** The highest 1-hr concentration amongst all 1-hr samples measured in the study is provided.

Table C 4. Hydrogen sulfide concentrations in urban areas

Sampling location/year(s)	Sampling regime	Average*	99th percentile**	Maximum***, ****	Reference
Alberta (Lethbridge) September 1998–July 1999	Air measured hourly, sampled for 78 hours over 8-day period for 4 seasons at 5 locations	1 ppb (1.4 µg/m^3)	NA	0.6 ppb –3 ppb (0.84–4.2 µg/m^3)	Alberta Environment 2000a
Quebec (urban areas) 2002 – 2009	Air sampled continuously every hour at 4 sampling stations	0.9 ppb (1.25 µg/m^3)	NA	22 ppb (30.8 µg/m^3)	CESPA 2010
New Brunswick (Saint John) August 4, 2013–August 11, 2016	Continuous hourly sampling at 2 sites, reporting for total reduced sulfur (Forest Hills & West Side)	NA	0.6 and 1.2 ppb (0.84 and 1.68 µg/m^3) West Side and Forest Hills, respectively	10.8 ppb (15.12 µg/m^3)	New Brunswick 2016

Sampling location/year(s)	**Sampling regime**	**Average***	**99th percentile****	**Maximum***, ******	**Reference**
New Brunswick (Saint John) August 11, 2016–April 9, 2019	Continuous hourly sampling at 2 sites, reporting for total reduced sulfur (Forest Hills & West Side)	0.23 ppb (0.32 µg/m^3)	0.6 ppb and 1.1 ppb (0.84 µg/m^3 and 1.7 µg/m^3) West Side and Forest Hills, respectively	5.52 ppb (7.7 µg/m^3) Forest Hills	New Brunswick 2019
Southwestern Ontario (Sarnia)***** 2014–2015	Continuous annual average, maximum 24-hr and max 1-hr sampling at 3 stations (for total reduced sulfur)	Annual: 0.12 ppb –0.48 ppb (0.17 µg/m^3 – 69 µg/m^3)	NA	1-hr 2.4 ppb –12.0 ppb (3.4 µg/m^3 – 17 µg/m^3); 24-hr 0.78 ppb – 1.2 ppb (1.1 µg/m^3 – 1.7 µg/m^3)	OMECC 2017

* Typically, an average of all hourly samples over the sampling period is calculated for each station in the study or database; the highest average amongst stations is provided here.

** 99th percentiles of hourly samples over the sampling period are calculated for each monitoring station in the study; the highest 99th percentile is provided here.

*** The highest 1-hr concentration amongst all 1-hr samples measured in the study is provided.

****: Concentrations were converted under the assumption that hydrogen sulfide accounts for up to 60% of total reduced sulfur (Environment Canada 2004b).

*****: Aamjiwnaang First Nation community, located within a heavily industrialized area south of Sarnia, ON.

Table C-5. Hydrogen sulfide concentrations near livestock operations

Sampling location/year(s)	Sampling regime	Average*	99th percentile **	Maximum***	Reference
Alberta October 2008–December 2009	Air measured continuously for a minimum of 15 days upwind and downwind of a livestock operation	Median 0.63 ppb (0.90 µg/m^3) Station 1 Median 0.62 ppb (0.89 µg/m^3) Station 2	NA	0.49–6.59 ppb (0.70 – 9.5 µg/m^3) Station 1 0.68–22.8 ppb (0.98–32.85 µg/m^3) Station 2	Alberta Government 2011
Alberta (Girouxville) October 2007–September 2008	Continuous	Median 1-hr 0.55 ppb (0.79 µg/m^3)	NA	14.9 ppb (21 µg/m^3)	PASZA 2011
Alberta (livestock operations near Lethbridge) September 1998–July 1999	Air sampled during a 10-day period over 4 seasons, sampled continuously every hour at 17 sites located downwind of livestock operations near Lethbridge and Warner	26 ppb (36.4 µg/m^3) at site #12 15 of the 17 sites averaged 5 ppb or lower	NA	54 ppb (76 µg/m^3) Within 30 meters of source, near a hogfarm	Alberta Environment 2000b

Abbreviations: NA, not available; NS, not stated; TRS, total reduced sulfur

* Typically, an average of all hourly samples over the sampling period is calculated for each station in the study or database; the highest average amongst stations is provided here.

** 99th percentile of hourly samples over the sampling period are calculated for each monitoring station in the study; the highest 99th percentile is provided here.

*** The highest 1-hr concentration amongst all 1-hr samples measured in the study is provided.

Table C-6. Hydrogen sulfide concentrations near mixed-use sources of exposure

Sampling location/year (s)	Sampling regime	Average*	99th percentile **	Maximum ***	Reference
Alberta (Edmonton) 2014	Continuous 1-hr sampling at 5 stations	<1 ppb – 1 ppb (<1.4-1.4 µg/m^3), max annual average	NA	22 ppb (30.8 µg/m^3) Max 24-hr average: 3 ppb (4.2 µg/m^3)	ACA 2014
Alberta (multiple stations) January 1, 2016–December 31, 2017	Continuous 1-hr sampling at all stations that monitor hydrogen sulfide	0.03 ppb – 0.5 ppb (0.04 ug/m^3–0.7 ug/m^3)	7 ppb (9.8 ug/m^3) Calgary Southeast station	86 ppb (120 ug/m^3) Mannix station, April 28, 2017	AEP 2018
Saskatchewan 2018	Continuous monitoring	0.6 ppb –0.9 ppb (0.86 µg/m^3 –1.3 ug/m^3) annual average	NA	11.2 ppb – 18.5 ppb (16.14 µg/m^3 – 26.6 ug/m^3) 1-hr max 1.8 ppb – 3.7 ppb (2.6 µg/m^3 –5.33 ug/m^3) 24-hr max	GPAZ 2018
Saskatchewan 2016	Continuous at 4 monitoring stations	0.2 ppb –0.5 ppb (0.28 µg/m^3 – 0.72 ug/m^3) annual average	NA	24-hr average: 3.7–3.88 ppb (5.33–5.47 ug/m^3) Max 1-hr average: 21.4–26.0 ppb (30.84–	WYAMZ 2016, 2018

				37.47 ug/m^3)	
Saskatchewan (southeastern) 2015	Continuous 1-hr sampling at 5 sites	1.4 ppb (1.96 µg/m^3) (annual)	NA	118.6 ppb (166.0 µg/m^3) at Wauchope station on August 1, 2015, 5:00 am Max 24-hr average: 14.0 ppb (19.6 µg/m^3) at Wauchope station	SESAA 2015
Saskatchewan (Western Yellowhead Air Management Zone, WYAMZ) 2014	Air sampled continuously every hour at 2 locations (Maidstone and Kindersley)	0.2 ppb and 0.3 ppb (0.28 and 0.42 µg/m^3) Annual average for Kindersley and Maidstone stations, respectively	NA	13.5 ppb (18.9 ug/m3) at Maidstone Max 24-hr average: 2.3 ppb (3.22 µg/m^3) at Maidstone	AMEC 2014

* Typically, an average of all hourly samples over the sampling period is calculated for each station in the study or database; the highest average amongst stations is provided here.

** 99th percentiles of hourly samples over the sampling period are calculated for each monitoring station in the study; the highest 99th percentile is provided here;

*** The highest 1-hr concentration amongst all 1-hr samples measured in study is provided.

Appendix D. Summary of incidental exposure data

A summary of the information obtained on incidental releases of hydrogen sulfide is provided in Table D 1 and Table D 2 below. The tables below describe measured data, mainly from inactive wells, on reported levels of hydrogen sulfide.

Table D 1. Reports of incidental releases of hydrogen sulfide in proximity of urban areas or rural communities in Ontario and Saskatchewan

Sampling location and sampling time	Sampling approach	Concentrations
Haldimond and Norfolk County, Ontario[a] August 9–16, 2017	Monitoring at two locations on a private property containing an inactive sour natural gas well that is a source of hydrogen sulfide. Sampling was carried out at the barn on the property and at the residence, which were located 90 and 150 m from the well, respectively.	H_2S peak (10-min average): Barn: 6 ppm Residence: 2 ppm H_2S 8-hr average: Barn: 0.57 ppm Residence: 0.56 ppm
Haldimond and Norfolk County, Ontario[b] August 24–29, 2018	Monitoring (1-min intervals) was carried out at varying locations near an inactive sour gas well on a residential property. Four monitors were used during the sampling period and were periodically moved to measure concentrations at different areas on or near the residence where the well was located. The exact location of the well could not be determined as it was located under a wetland. Information on the monitoring equipment used to measure H_2S concentrations was not provided.	Levels of H_2S from the period of August 24–29, 2018, ranged from 0–180 ppm. A summary of median and 95th percentile concentrations from each monitor is presented below: Monitor 1 (at the residence, approx. 525 m from well): Median: 0 ppm 95th percentile: 0 ppm Monitor 2 (approx. 75 m from well): Median: 0 ppm 95th percentile: 4 ppm

Sampling location and sampling time	**Sampling approach**	**Concentrations**
		Monitor 3* (approx. 60 m from well): Median: 6 ppm 95th percentile: 29 ppm Monitor 4 (at the assumed well): Median: 0 ppm 95th percentile: 2 ppm **Note: Data collected from August 26–29, 2018. Measurements from August 24 and 25 were not available.*
Various locations throughout southern Ontario, at 43 wells[c] 2010–2018	Compiled data from field inspection reports from the Ontario Ministry of Natural Resources and Forestry. A total of 65 point-in-time measurements were obtained from field inspections of 43 inactive wells releasing hydrogen sulfide.* * *Note: These measurements were taken with equipment used by Petroleum Inspectors for the personal safety of workers conducting field activities for the early detection and monitoring of H_2S levels(and other gases). This equipment records point-in-time gas concentrations in the breathing zone. Specifications for personal gas monitors used by inspectors:* *Model(s): GX-2009 Personal Multi Gas Monitor / GX-2012 Handheld Multi Gas Monitor*	H_2S levels in the 65 inspection reports: 59/65: >2ppm 24/65: 10–100 ppm 16/65: ≥100 ppm

Sampling location and sampling time	Sampling approach	Concentrations
	H_2S Detection Range: 0–100 ppm *Alarm Setting(s): Inspectors have the alarm engaged to sound at 5 ppm. At this level, inspectors terminate the inspection and leave the site immediately.*	
Oxbow, Saskatchewan[d] October 30, 2012	Point-in-time measurement was taken by a private citizen in response to a teenager showing serious health effects; she pulled the teen inside, grabbed an air monitor and held it out the door. A plume of sour gas had likely migrated onto her property, resulting in adverse health effects. Details on the air monitor used to capture reading were not provided.	Measured concentration of H_2S: >100 ppm

[a] Personal communication, email from the Ministry of Environment and Climate Change, Government of Ontario, to the Existing Substances Risk Assessment Bureau, Health Canada, dated April 2018; unreferenced.
[b] Personal communication, emails from the Haldimand-Norfolk Health and Social Services, to the Existing Substances Risk Assessment Bureau, Health Canada, dated February 2019; unreferenced.
[c] Personal communication, email from MNRF, Government of Ontario, to the Existing Substances Risk Assessment Bureau, Health Canada, dated June 6, 2018; unreferenced.
[d] Cribb 2017

Reports of incidental releases of hydrogen sulfide were also obtained from the Ontario Ministry of Environment, Conservation, and Parks, Spills Action Centre. A total of 6 incidents for which levels of hydrogen sulfide were measured in close proximity to the general population are summarized in Table D 2 below. Data on the equipment, sampling method, and distance to the H_2S source, which were used to measure the substance during these incidents, were not provided (MOECP 2019).

Table D 2. Reports of incidental releases of hydrogen sulfide from the Ontario Ministry of Environment, Conservation and Parks, Spills Action Centre

Location of incidental exposure and date	Incidental exposure report details
November 2012 Windsor, Ontario	Caller reported that they had struck an old abandoned well, which had exposed H_2S bubbling up in the water being discharged. Caller stated that it was a 2" steel casing well, but it was unknown what type of well it was. Caller added that the water was flowing from the bedrock and there was inconsistent bubbling of H_2S. Caller reported that they had tested the atmosphere at the source of the well, and the highest H_2S reading was 15ppm, which then dispersed fairly quickly. At the time of the call, they were trying to fix the well with a stand pipe to prevent further bubbling and discharge. They would try to properly decommission it next week by hiring a consultant/contractor. There was a residential area near them that might notice an odour. Houses within 300 m. Caller stated that the area may have been exposed over a day or so ago; staff had not relayed information regarding the odour prior to today.
October 2014 Windsor, Ontario	Caller reported an ongoing release of hydrogen sulfide gas and black liquor from an artesian well on their job site, located approximately 100 metres northeast of the intersection. Caller reported that the release was discovered at 16:15, within a hole that was 10 metres deep from excavation. Caller reported that, at the time of the call, the gas was contained within their excavation area and that they were bordering off the area, removing employees, and bringing someone in to cap the well. Caller reported that there were residences nearby within 100 metres of the site and that they were getting a gas reading of 20 ppm. Caller reported that this was enough to produce a notable odour, which would not be a problem if exposure was brief, but if long term exposure occurred, it could become a concern. Caller requested that the Windsor District Office contact them. 17:08: Windsor District Office to Spills Action Centre (SAC). Caller reported that they had spoken with the construction company and confirmed that the artesian well was releasing black liquor and hydrogen sulfide, and reported two readings of 8 ppm and 20 ppm. Caller confirmed that the construction company had removed the employees from the area and were currently monitoring the gas levels. Caller reported that the black liquor was not a concern in terms of environmental impacts as

Location of incidental exposure and date	Incidental exposure report details
	the material was contained within the 10 metre deep hole, surrounded by clay soil, and its spread would stop when the contractor capped it. Caller requested that the Ministry of Labour (MOL) be informed as the location was a worksite and the threshold for hydrogen sulfide gas is 2 ppm.
October 2016 Leamington, Ontario	14:10: Declaration of emergency from Municipality of Leamington. 14:10: Received by OFM/ PEOC. Caller reported a hydrogen sulfide leak from an old, 150-year-old well that was not capped. This well was located between two homes in a residential area. Shelter-in-place for nearby community residents. Well located in Leamington. The MNRF was responding to the incident. The Fire Department had a crew on site for rotating 3-hour shifts and would continue to do so. Representatives of the well-owner were also on site. 16:36: Three residences were affected by the shelter-in-place order/advisory that had been put in place. The residences were advised to turn off ventilation systems, close windows, and stay inside as a precautionary measure. It was determined that the site did not contain a historic petroleum well but possibly a water well. The MNRF and their consultants would cap the well and monitor for gas in the surrounding homes for a period of time.
January 2010 Norfolk County, Ontario	Caller reported natural gas and H_2S bubbling up through a creek (name unknown). Cause was unknown at the time of the call. The Ministry of Natural Resources (MNR) was trying to determine well ownership (it may have been an abandoned well) so that the responsible party could arrange an appropriate remedy to the situation. No signs of impact on wildlife in the area. 2010-02-01: It was suspected that work may have been done on the well so that it would drain directly into the creek, instead of having sulfur water from the gas-bearing layer pool on the ground. Well located on east side of creek, 100 m south of the bridge

Location of incidental exposure and date	Incidental exposure report details
	Well casing seen on a 45 degree angle, >100 ppm H_2S at top of casing H_2S bubbling up under tree—ice
January 2005 Waterloo, Ontario	Caller reported a complaint of a sulphurous odour at a Kitchener-Waterloo school. Odour was from sewer gas drawn in from stacks on the building's roof to air intake for the heating system. Region had first been notified on 2005-01-06 at 14:30 and again the next day. School was located in close proximity to a landfill site, and the city had had problems before. The landfill leachate collection system discharges into the sewer system. No traces of H_2S or CO in the school's heating system. Region would extend sewer stack upwards of 2.4 m. HU would be notified by Region. There were an estimated 300 students in the elementary school. The stacks were roof vent stacks for the building's plumbing system and were connected to the sanitary sewers. City of Waterloo was aware of the situation. This had occurred before in different locations, although incidents were confined to private homes where traps had been left unmaintained. Solution: A force main leads from the LFS to a gravity-fed sewer; at the connection, there is a drop of 12 ft., which agitates the sewage. The school was about 500 m away from this drop. At the school, sewer vents were about 1 ft. off the roof, and the roofline had a wall that acted as a barrier for air dispersion. Air intakes for the building were close to the sewer vents, as noted above. To alleviate the problem, the Region installed vent stack extensions, two at 8 ft. and one at 10 ft., on January 5.
May 2011 Sarnia, Ontario	Caller reported that the Sarnia MOE District Office had contacted the company in Sarnia that afternoon about a sulphur odour complaint they had received. Company was investigating the complaint at the time of the call and would keep the SAC updated. Caller did not know which area of Sarnia the complaint had come from. A level of 3 ppm for H_2S was detected at their fence line. A code 6 was put in place, and the street was closed down. Suspected source was at the company tank. A hot material had been placed in the tank, which could have caused

Location of incidental exposure and date	Incidental exposure report details
	the problem. Tank was now isolated. Readings at the fence line were now showing 0 for H_2S. Company was continuing to monitor the situation.