6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Hydrogen sulfide has been found in at least 34 of the 1,832 waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) and carbonyl sulfide was detected in at least 4 of the 1,832 waste sites (ATSDR 2015). However, the number of sites evaluated for these substances is not known and hydrogen sulfide and carbonyl sulfide are ubiquitous in the atmosphere. The frequency of these sites can be seen in Figures 6-1 and 6-2.

Carbonyl sulfide and hydrogen sulfide are principal components in the natural sulfur cycle. Bacteria, fungi, and actinomycetes (a fungus-like bacteria) release hydrogen sulfide during the decomposition of sulfur containing proteins and by the direct reduction of sulfate (SO_4^{2-}). Hydrogen sulfide is also emitted from volcanoes, stagnant or polluted waters, and manure or coal pits with low oxygen content (Aneja 1990; Khalil and Ramussen 1984). The majority of carbonyl sulfide that enters the environment is released to air and it is very abundant in the troposphere (Conrad and Meuser 2000; EPA 1994c, 1994d; Meinrat et al. 1992; Simmons et al. 2012; Stimler et al. 2010). It enters the atmosphere from both natural and anthropogenic sources (EPA 1994c, 1994d; Meinrat et al. 1992; Stimler et al. 2010). Carbonyl sulfide is released from wetlands, salt marshes, soil, oceans, deciduous and coniferous trees, and volcanic gases (Blake et al. 2004; EPA 1994c, 1994d; Meinrat et al. 1992; Rasmussen et al. 1982a, 1982b; Stimler et al. 2010). Anthropogenic sources of carbonyl sulfide include production as a chemical intermediate; burning of biomass; oxidation of carbon disulfide and dimethyl sulfide; aluminum production; combustion of coal; extraction of natural gas and petroleum crude oil; recovery of sulfur; combustion of garbage and plastics; manufacture of synthetic fibers, starch, and rubber; fish processing; and automobiles (ASTM International 2012; Blake et al. 2004; EPA 1994c, 1994d; PERC 2001). Natural sources of carbonyl sulfide and hydrogen sulfide are significantly greater than anthropogenic emissions.

Carbonyl sulfide can be removed from the atmosphere by terrestrial vegetation, soils, photolysis, and reaction with hydroxyl and oxygen radicals (Blake et al. 2004; EPA 1994d; Stimler et al. 2010). Decomposition of carbonyl sulfide by moisture results in the formation of carbon dioxide and hydrogen sulfide. Hydrogen sulfide is consumed by bacteria found in soil and water that oxidize hydrogen sulfide to elemental sulfur. Photosynthetic bacteria can oxidize hydrogen sulfide to sulfur and sulfate in the presence of light and the absence of oxygen (EPA 1993; WHO 1981).

Figure 6-1. Frequency of NPL Sites with Hydrogen Sulfide Contamination

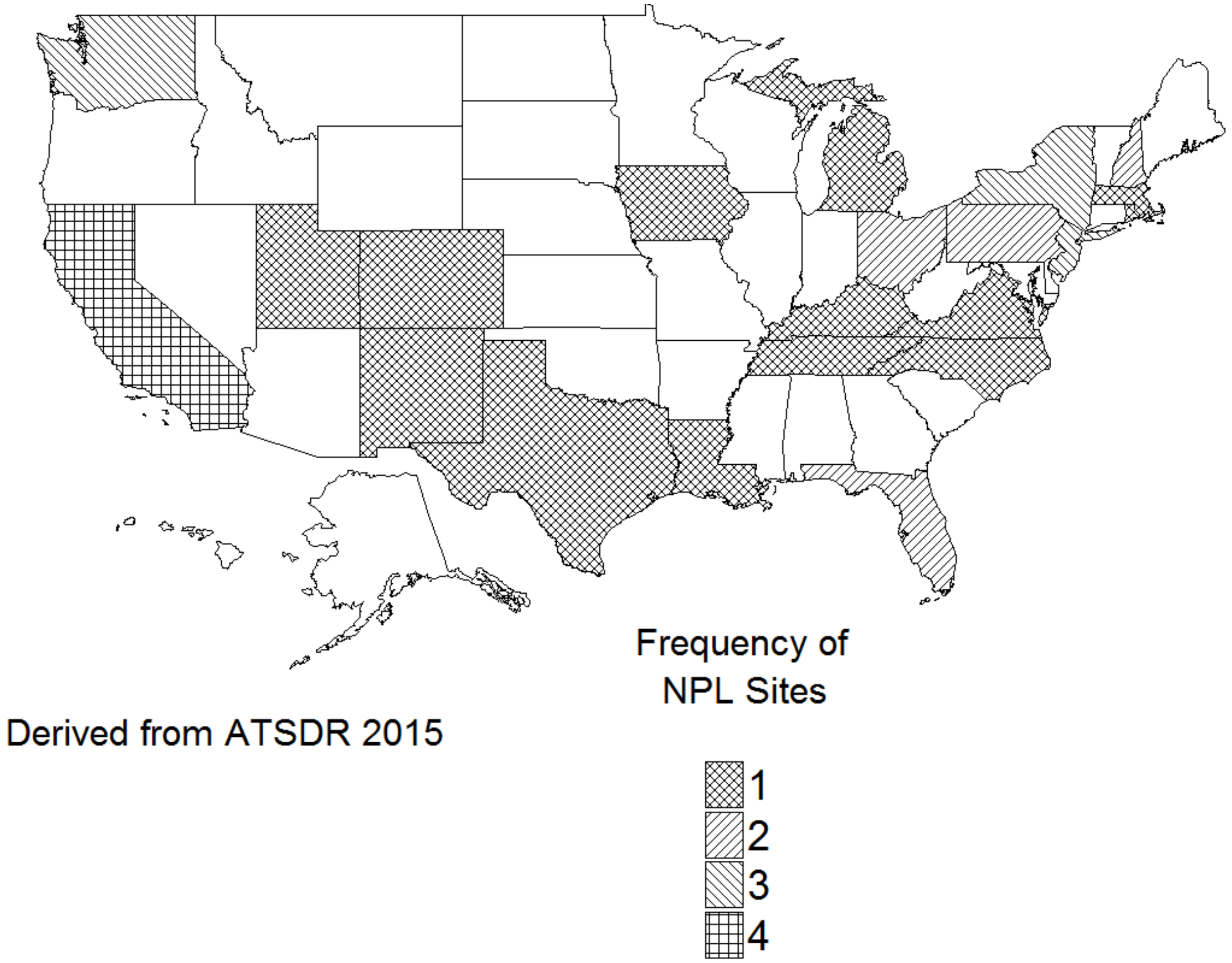
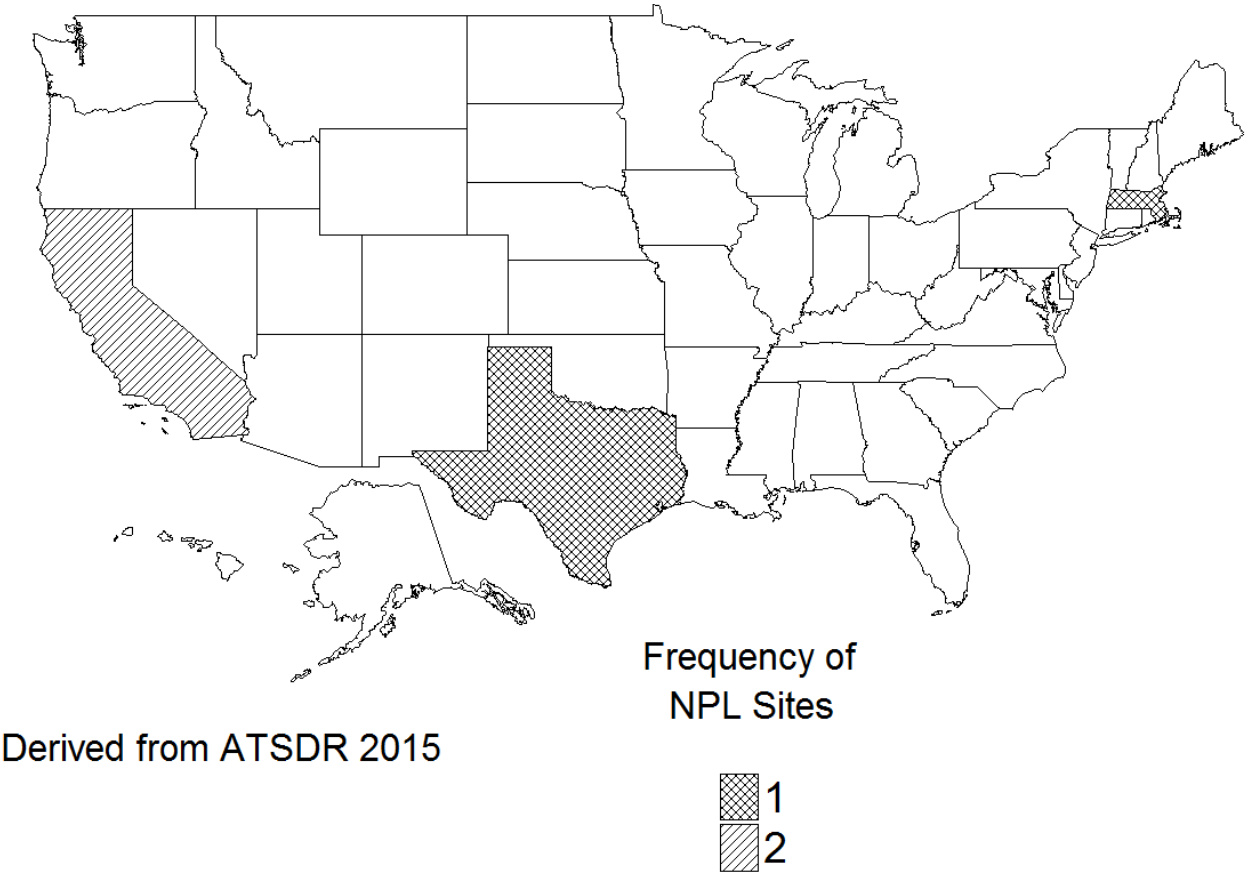


Figure 6-2. Frequency of NPL Sites with Carbonyl Sulfide Contamination



Derived from ATSDR 2015

Degradation of hydrogen sulfide in the atmosphere can occur through oxidation by oxygen (O_2) and ozone (O_3) to yield sulfur dioxide (SO_2), and ultimately, sulfate compounds. Sulfur dioxide and sulfates are eventually removed from the atmosphere through absorption by plants and soils or through precipitation (Hill 1973). Hydrogen sulfide in air can also react with photochemically generated hydroxyl radicals. The effective lifetimes for hydrogen sulfide based on summer daytime and yearly average hydroxyl radical concentrations have been estimated to be 0.23 and 2.3 days, respectively, based on a measured rate constant of 4.8×10^{-12} cm^3/molecule second (Cox 1975). Lifetimes in air ranging from approximately 1 day in the summer to 42 days in the winter have been estimated for hydrogen sulfide (Bottenheim and Strausz 1980). Hydrogen sulfide is not expected to be decomposed by direct absorption of ultraviolet radiation, and its reaction with ozone is not expected to be a significant environmental fate (Cox 1975).

Hydrogen sulfide oxidation by O_2 may readily occur in surface waters (Millero et al. 1987, 1989). Hydrogen sulfide is readily soluble in water. In aqueous solution, hydrogen sulfide is a weak acid, exhibiting two acid dissociation constants. The first dissociation yields bisulfide ion (HS^-), and the second yields sulfide ion (S^{2-}), with pK_a values for each of these dissociations of 7.04 and 11.96, respectively (O'Neil et al. 2001). At a pH of 7.0, the ratio of the concentration of aqueous hydrogen sulfide to bisulfate ion is approximately 1-to-1. As the pH increases above 7.0, the ratio of the concentration of bisulfide ion to aqueous hydrogen sulfide increases. Only above pH 12 will the concentration of sulfide ion become significant (>50%). Hydrogen sulfide has been shown to sorb to various soils (Cihacek and Bremner 1993; Smith et al. 1973). Several species of soil, aquatic, and marine microorganisms oxidize hydrogen sulfide to elemental sulfur, and its half-time in these environments usually ranges from 1 hour to several hours (Jørgensen 1982). Because it is a gas under ambient conditions, bioconcentration and food chain biomagnification are unlikely.

While carbonyl sulfide is relatively inert in the troposphere, with a reported lifetime ranging from 2 to 10 years (Blake et al. 2004; EPA 1994d; Liu et al. 2007; Meinrat et al. 1992; Stimler et al. 2010), it is transported to the stratosphere where it undergoes photolysis and reaction with oxygen and photochemically-produced hydroxyl radicals (EPA 1994d; Meinrat et al. 1992; Stimler et al. 2010). It may contribute to ozone depletion (Conrad and Meuser 2000; Liu et al. 2007; Meinrat et al. 1992; Simmons et al. 2012).

Carbonyl sulfide can enter water and soil through atmospheric deposition. In water, carbonyl sulfide reacts with the water to form carbon dioxide and hydrogen sulfide. It is expected to rapidly volatilize to air. Carbonyl sulfide does not bind to soils and may be transported to groundwater (EPA 1994c; Meinrat et al. 1992;). While soils could potentially be both a sink and a source to the atmosphere, recent data indicate that soils are primarily a sink for atmospheric carbonyl sulfide (Conrad and Meuser 2000; Kato et al. 2008; Liu et al. 2007, 2010; Simmons et al. 2012; Stimler et al. 2010). Carbonyl sulfide has been found to biodegrade in soils (Kato et al. 2008). It is not expected to bioconcentrate in aquatic organisms (EPA 1994c, 1994d).

Exposure of the general population to hydrogen sulfide and carbonyl sulfide is primarily through inhalation of ambient air, as these substances are ubiquitous in the atmosphere. Occupational exposure to carbonyl sulfide is primarily a result of its production and use as a chemical intermediate (EPA 1994d) and its production as a byproduct in petroleum refining and coal distillation (EPA 1994c). Occupational exposure to hydrogen sulfide occurs at facilities where it is produced, used, or generated such as petroleum refineries, natural gas plants, petrochemical plants, coke oven plants, kraft paper mills, viscose rayon manufacturing plants, sulfur production plants, iron smelters, food processing plants, manure treatment facilities, landfills, textile plants, waste water treatment facilities, and tanneries (Chénard et al. 2003; Devai and DeLaune 1999; Lehman 1996; Rimatori et al. 1996; Svendsen 2001).

6.2 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ 10 or more full-time employees; if their facility is included in the following Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes ≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 2005).

6.2.1 Air

Hydrogen Sulfide. Estimated releases of 20.6 million pounds (~9,331 metric tons) of hydrogen sulfide to the atmosphere from 516 domestic manufacturing and processing facilities in 2014, accounted for about 79% of the estimated total environmental releases from facilities required to report to the TRI (TRI14 2015). These releases are summarized in Table 6-1.

Hydrogen sulfide is produced naturally and as a result of human activity. Natural sources, such as swamps, bogs, and volcanoes, account for about 90% of the total amount of hydrogen sulfide in the atmosphere (EPA 1993). Annually, 100–324 million tons of hydrogen sulfide are released from natural sources with half from volcanoes, flooded ground, or hydrogeological sources, and the other half from the oceans (Pouliquen et al. 1989). Massive release of hydrogen sulfide to the ocean surface and atmosphere could occur during intervals of ocean anoxia (Kump et al. 2005). Nearshore hydrogen sulfide eruptions occur in the Atlantic Ocean along the central coast of Nambia and have been observed to affect areas of ocean surface of >20,000 km^2 (Weeks et al. 2004). Many petroleum deposits and natural gas wells also contain hydrogen sulfide ("sour-gas wells") and become sources of atmospheric hydrogen sulfide release when developed (Layton and Cederwall 1986; Leahey and Schroeder 1986). Hydrogen sulfide is emitted by some plant species as a byproduct of sulfite metabolism (Takemoto et al. 1986; Wilson et al. 1978). Emission rates of various biogenic sulfur gases (including hydrogen sulfide) from the exposed soils of five wetland plant communities in Florida were measured during April, May, and October 1985 and January 1986. Emission rates for hydrogen sulfide varied from 0.1–1.0 to 8.3–152 μg sulfur/m^2/hour from a spike grass site in the Everglades National Park in January 1986 and a sawgrass site at Merritt Island National Wildlife Refuge in April 1985, respectively (Cooper et al. 1987). Hydrogen sulfide was identified in the volatile emissions of leaf litter of poplar trees (*Populus balsamifera*) (Isidorov and Jdanova 2002). Estimates of the terrestrial emission rates of hydrogen sulfide range from 58 to 110 million tons of sulfur/year and estimates of the emission rates from oceans range from 30 to 170 million tons of sulfur/year (Hill 1973).

Facilities where hydrogen sulfide is produced, used, or generated include petroleum refineries, natural gas plants, petrochemical plants, coke oven plants, kraft paper mills, viscose rayon manufacturing plants, sulfur production plants, iron smelters, food processing plants, manure treatment facilities, landfills,

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Hydrogen Sulfide[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
AK	2	4,141	30	0	66	0	4,237	0	4,237
AL	30	2,231,120	88,145	0	11,612	0	2,330,877	No data	2,330,877
AR	16	1,420,286	21,236	0	62,507	0	1,504,029	No data	1,504,029
CA	21	144,986	449	0	0	0	145,435	0	145,435
CO	3	7,307	0	0	0	0	7,307	No data	7,307
DE	4	28,932	1	0	0	0	28,932	No data	28,932
FL	12	538,399	2,759	0	1,559	17,300	542,213	17,804	560,017
GA	22	2,289,315	120,324	0	4,416	0	2,414,055	No data	2,414,055
HI	2	1,802	0	0	0	0	1,802	No data	1,802
IA	9	104,506	1,713	0	3,838	4	106,219	3,842	110,061
ID	4	168,257	579	0	170	0	169,006	No data	169,006
IL	18	197,020	4,221	0	93	0	201,276	58	201,334
IN	13	338,570	120	0	1	1	338,690	2	338,692
KS	10	161,492	0	0	0	7,054	161,492	7,054	168,546
KY	9	239,157	537	0	0	0	239,694	No data	239,694
LA	45	1,345,124	9,245	1,554	2,018	0	1,357,941	0	1,357,941
MA	2	3	0	0	0	0	3	No data	3
MD	3	178,383	0	0	0	0	178,383	No data	178,383
ME	6	474,012	583	0	243	0	474,671	167	474,838
MI	6	91,713	230	0	277	0	92,220	No data	92,220
MN	9	377,654	13	0	23	0	377,667	23	377,690
MO	7	9,030	34	0	1,012	0	9,069	1,007	10,076
MS	13	666,188	142,915	0	0	0	809,103	No data	809,103
MT	6	58,200	131	0	5	0	58,331	5	58,336
NC	11	2,377,504	4,345	0	1,177	0	2,381,917	1,109	2,383,026
ND	6	1,248,744	73,100	1,200	0	2,649	1,323,044	2,649	1,325,693
NE	8	51,636	13,734	0	475	0	65,370	475	65,845
NJ	5	10,977	80	0	0	0	11,057	No data	11,057
NM	6	151,533	0	4,285,492	15,798	1	4,449,859	2,965	4,452,824
NV	1	0	No data	0	0	0	No data	No data	No data
NY	7	35,432	368	0	39	0	35,800	39	35,839
OH	20	110,595	71	0	813	0	110,689	790	111,479
OK	11	189,841	1,682	0	475	0	191,998	No data	191,998
OR	6	275,279	19,438	0	45	0	294,762	No data	294,762
PA	14	331,129	2,920	0	192	0	334,241	1	334,241
PR	4	112,781	0	0	0	0	112,781	No data	112,781

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Hydrogen Sulfide[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
SC	8	682,435	13,287	0	54,959	0	750,681	No data	750,681
SD	2	982	0	0	1	0	982	1	983
TN	11	1,109,099	1,969	0	0	0	1,111,068	0	1,111,068
TX	75	1,677,195	8,134	203,354	196,884	0	2,085,369	197	2,085,567
UT	5	18,117	0	0	260	0	18,377	No data	18,377
VA	8	404,915	165	0	12,098	0	416,147	1,031	417,177
WA	16	389,526	7,084	0	872	0	397,379	103	397,482
WI	13	279,032	3,347	0	2,698	0	283,201	1,876	285,077
WV	2	3,462	33	0	0	0	3,495	No data	3,495
WY	5	34,792	7	0	192	13,000	34,850	13,141	47,991
Total	516	20,570,603	543,028	4,491,600	374,818	40,009	25,965,719	54,339	26,020,057

[a] The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b] Data in TRI are maximum amounts released by each facility.
[c] Post office state abbreviations are used.
[d] Number of reporting facilities.
[e] The sum of fugitive and point source releases are included in releases to air by a given facility.
[f] Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g] Class I wells, Class II-V wells, and underground injection.
[h] Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i] Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown.
[j] The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k] Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI14 2015 (Data are from 2014)

textile plants, waste water treatment facilities, and tanneries (Beck et al. 1981; Chénard et al. 2003; Devai and DeLaune 1999; Grant and Schuman 1993; Lehman 1996; Rimatori et al. 1996; Sittig 2002; Svendsen 2001). Hydrogen sulfide is also used as an agricultural disinfectant, in the production of heavy water, and as an additive in lubricants and cutting oils (Bingham et al. 2001; Sittig 2002; Weil and Sandler 1997). Hydrogen sulfide may also be encountered in various industrial processes including the manufacture of dyes and pigments, felt, artificial silk, farming; in brewing, glue making, and rubber vulcanization; and in lithography and photoengraving (Beck et al. 1981; Grant and Schuman 1993; Sittig 2002). Accidental release or improper disposal of materials resulting from these processes may result in hydrogen sulfide emissions. Ambient hydrogen sulfide concentrations in the air near landfills indicate that they are a source as well (ATSDR 2015). Sulfides, including hydrogen sulfide, constitute up to 1% by volume of typical landfill gases (ATSDR 2001b). The Fresh Kills Landfill on Staten Island, New York has been estimated to release approximately 16 tons of hydrogen sulfide to the air annually (ATSDR 2000). Facilities that treat manure may also release hydrogen sulfide to the air. Hydrogen sulfide emissions were measured from two anaerobic lagoons used for treating swine waste; the overall mean hydrogen sulfide release was 5.7 μg/m^2/second (Lim et al. 2003).

Carbonyl Sulfide. Estimated releases of 14.2 million pounds (~6,439 metric tons) of carbonyl sulfide to the atmosphere from 136 domestic manufacturing and processing facilities in 2014, accounted for about 99% of the estimated total environmental releases from facilities required to report to the TRI (TRI14 2015). These releases are summarized in Table 6-2.

Section 112(b) of the Clean Air Act (CAA) lists carbonyl sulfide as one of 188 hazardous air pollutants (HAPs) (hydrogen sulfide was initially listed as well but since has been removed) known or suspected to cause cancer or other serious human health effects or ecosystem damage (EPA 2009d). EPA's National Emission Inventory (NEI) database contains data regarding sources that emit criteria air pollutants and their precursors, and HAPs for the 50 United States, Washington DC, Puerto Rico, and the U.S. Virgin Islands (prior to 1999, criteria pollutant emission estimates were maintained in the National Emission Trends [NET] database and HAP emission estimates were maintained in the National Toxics Inventory [NTI] database). The NEI database derives emission data from multiple sources including state and local environmental agencies, the TRI database, computer models for on-road and off-road emissions, and databases related to EPA's Maximum Achievable Control Technology (MACT) programs to reduce emissions of HAPs. Data downloaded from the 2008 and 2011 NEI indicated that the total emission of carbonyl sulfide was approximately 25.5 million pounds and 20.7 million pounds respectively, with the

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Carbonyl Sulfide[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
AK	1	560	0	0	No data	No data	560	No data	560
AL	4	134,764	0	0	No data	No data	134,764	No data	134,764
AR	1	528	0	0	No data	No data	528	No data	528
CA	14	41,451	0	0	No data	No data	41,451	No data	41,451
DE	2	225,270	0	0	No data	No data	225,270	No data	225,270
HI	1	1,200	0	0	No data	No data	1,200	No data	1,200
IL	6	25,184	0	0	No data	No data	25,184	No data	25,184
IN	7	1,051,022	0	0	No data	No data	1,051,022	No data	1,051,022
KS	6	22,621	0	0	No data	80,159	22,621	80,159	102,780
KY	3	1,079,995	0	0	No data	No data	1,079,995	No data	1,079,995
LA	19	336,082	964	0	84	No data	337,046	84	337,130
MI	1	5	0	0	No data	No data	5	No data	5
MN	3	7,749	0	0	No data	No data	7,749	No data	7,749
MO	1	684,433	0	0	No data	No data	684,433	No data	684,433
MS	3	668,093	0	0	No data	No data	668,093	No data	668,093
MT	4	1,609	0	0	No data	No data	1,609	No data	1,609
ND	2	13,172	0	0	No data	No data	13,172	No data	13,172
NM	1	0	0	0	No data	No data	0	No data	0
NV	1	820	0	0	No data	No data	820	No data	820
NY	2	501,600	0	0	No data	No data	501,600	No data	501,600
OH	6	4,556,761	0	0	No data	No data	4,556,761	No data	4,556,761
OK	4	1,041	0	0	No data	No data	1,041	No data	1,041
PA	2	110,060	0	0	No data	No data	110,060	No data	110,060
SC	2	757,134	0	0	No data	No data	757,134	No data	757,134
TN	3	2,750,367	0	0	No data	No data	2,750,367	No data	2,750,367
TX	25	145,404	0	5	No data	No data	145,409	No data	145,409
UT	3	804	0	0	0	No data	804	0	804
WA	6	993,299	0	0	No data	No data	993,299	No data	993,299

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Carbonyl Sulfide[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
WI	1	202	0	0	No data	No data	202	No data	202
WY	2	3,636	0	0	No data	No data	3,636	No data	3,636
Total	136	14,114,864	964	5	84	80,159	14,115,834	80,243	14,196,077

[a] The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b] Data in TRI are maximum amounts released by each facility.
[c] Post office state abbreviations are used.
[d] Number of reporting facilities.
[e] The sum of fugitive and point source releases are included in releases to air by a given facility.
[f] Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g] Class I wells, Class II-V wells, and underground injection.
[h] Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i] Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown
[j] The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k] Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI14 2015 (Data are from 2014)

biggest source arising from chemical manufacturing and oil and gas production (EPA 2013f, 2015a). Since hydrogen sulfide has been removed from the list of HAPs, no data exists for it in the NEI. The 2011 NEI data are summarized in Table 6-3.

The vast majority of carbonyl sulfide that enters the environment is released into the air (EPA 1994c, 1994d). Of the sulfur-containing gases, carbonyl sulfide is the most abundant in the troposphere (Conrad and Meuser 2000; Meinrat et al. 1992; Simmons et al. 2012; Stimler et al. 2010). Carbonyl sulfide is a gas that can enter the atmosphere from both natural and anthropogenic sources (EPA 1994c, 1994d; Meinrat et al. 1992; Stimler et al. 2010). Natural sources account for the atmospheric release of approximately 4 billion pounds of carbonyl sulfide each year (EPA 1994c). Approximately 43% of atmospheric carbonyl sulfide is directly emitted from natural sources such as oceans, marshes, and volcanoes and an additional 35% derives from atmospheric transformation of carbon disulfide to carbonyl sulfide (Khalil and Rasmussen 1984). Thus, almost 80% of atmospheric carbonyl sulfide results from natural sources. Yearly emissions of carbonyl sulfide from oceans have been quantified as approximately $8x10^{11}$ gm/year (0.8 Tg/year) (Rasmussen et al. 1982a) and 12.7 Gmol/year (0.41 Tg sulfur/year) (Meinrat et al. 1992). Biomass burning and coal-fired power plants account for about 12 and 5% of anthropogenic emissions of carbonyl sulfide, respectively (Khalil and Rasmussen 1984). Other anthropogenic sources including titanium dioxide manufacturing, carbon black manufacturing, petroleum refining, aluminum producing, and mineral wool manufacturing in the United States and elsewhere account collectively for only approximately 4% of total carbonyl sulfide levels (Chin and Davis 1993).

The extraction of natural gas can result in the formation of carbonyl sulfide. When natural gas sources are saturated with water, hydrogen sulfide and carbon dioxide are formed (i.e., “sour gas”). These products undergo a hydrolysis reaction resulting in the formation of carbonyl sulfide and water. Using adsorbent materials for dehydration in this process is a significant factor in the creation of carbonyl sulfide (PERC 2001). Carbonyl sulfide is also found in the inlet gas to natural gas liquids recovery facilities, where it has a tendency to concentrate in the propane and propylene streams (ASTM International 2012; PERC 2001).

Blake et al. (2004) quantified the carbonyl sulfide emissions from various anthropogenic sources from different countries located in Asia. Ranges (and total emission) resulting from the combustion of various fuels were as follows (conversion factor is 1 Gg/year=1,000 metric tons/year): coal, 0.048–4.4 Gg/year

Table 6-3. 2011 National Air Emissions for Carbonyl Sulfide

Sector	Air emissions in pounds
Agriculture—livestock waste	0.112966
Fires—prescribed fires	45,594.35
Fires—wildfires	52,275.65
Fuel combustion—commercial/institutional—natural gas	0.002
Fuel combustion—commercial/institutional—other	17.36516
Fuel combustion—electric generation, natural gas	18.858
Fuel combustion—electric generation, other	227.5079
Fuel combustion—industrial boilers, ICEs, coal	6,300
Fuel combustion—industrial boilers, ICEs, natural gas	17,009
Fuel combustion—industrial boilers, ICEs, oil	2,503
Fuel combustion—industrial boilers, ICEs, other	10,776
Gas stations	5
Industrial processes—cement manufacturing	0
Industrial processes—chemical manufacturing	8,464,191
Industrial processes—not elsewhere classified	656,526
Industrial processes—non-ferrous metals	4,365,423
Industrial processes—oil and gas production	6,791,621
Industrial processes—petroleum refineries	221,201.6
Industrial processes—pulp and paper	44,543.54
Industrial processes—storage and transfer	28,305.36
Solvent—degreasing	21.1389
Solvent—industrial surface coating and solvent use	5,300.1
Waste disposal	21,188.27
Total	20,733,048

ICE = internal combustion engine

Source: EPA 2015a

(total emissions of 7.3 Gg/year); oil plants, 0.11–1.4 Gg/year (3.4 Gg/year); biofuel, 0.16–19.9 Gg/year (56.6 Gg/year); transport, 0.10–1.4 Gg/year (3.1 Gg/year); and biomass burning, 0.14–12.6 Gg/year (31.2 Gg/year). Emissions from industrial production ranged from 0.01 to 15.7 Gg/year (total emissions of 33.9 Gg/year, while landfills emissions were responsible for 0.0005–0.009 Gg/year (0.02 Gg/year). Agricultural sources included rice paddies, which had emissions ranging from 0.14 to 3.5 Gg/year (total emissions of 10.7 Gg/year), and animal feedlots, which had emissions ranging from 0.0002 to 0.006 Gg/year (total emissions of 0.01 Gg/year). The total anthropogenic emissions of carbonyl sulfide in Asia were determined to be 146 Gg/year (Blake et al. 2004).

6.2.2 Water

Hydrogen Sulfide. Estimated releases of 543,028 pounds (~246 metric tons) of hydrogen sulfide to surface water from 516 domestic manufacturing and processing facilities in 2014, accounted for about 2% of the estimated total environmental releases from facilities required to report to the TRI (TRI14 2015). These releases are summarized in Table 6-1.

Releases of hydrogen sulfide to water occur both naturally and as a result of human activity. Hydrogen sulfide released from aquatic plants or as a result of anaerobic chemical processes in swamps and bogs may dissolve in the water column or bind to clay or organic matter. Massive release of hydrogen sulfide to the ocean surface could occur during intervals of ocean anoxia (Kump et al. 2005).

Facilities where hydrogen sulfide is produced, used, or generated include petroleum refineries, natural gas plants, petrochemical plants, coke oven plants, kraft paper mills, viscose rayon manufacturing plants, sulfur production plants, iron smelters, food processing plants, manure treatment facilities, landfills, textile plants, waste water treatment facilities, and tanneries (Beck et al. 1981; Chénard et al. 2003; Devai and DeLaune 1999; Grant and Schuman 1993; Lehman 1996; Rimatori et al. 1996; Sittig 2002; Svendsen 2001). Hydrogen sulfide is also used as an agricultural disinfectant, in the production of heavy water, and as an additive in lubricants and cutting oils (Bingham et al. 2001; Sittig 2002; Weil and Sandler 1997). Hydrogen sulfide may also be encountered in various industrial processes including the manufacture of dyes and pigments, felt, and artificial silk; in farming, brewing, glue making, and rubber vulcanization; and in lithography and photoengraving (Beck et al. 1981; Grant and Schuman 1993; Sittig 2002). Discharge liquids from these and other activities can release hydrogen sulfide to receiving waters (EPA 1993).

Carbonyl Sulfide. Estimated releases of 964 pounds (~0.44 metric tons) of carbonyl sulfide to surface water from 136 domestic manufacturing and processing facilities in 2014, accounted for <1% of the estimated total environmental releases from facilities required to report to the TRI (TRI14 2015). These releases are summarized in Table 6-2.

Carbonyl sulfide is a gas and is therefore primarily released to water through atmospheric deposition. When released to water, carbonyl sulfide will dissolve and may react with the water to form hydrogen sulfide (EPA 1994c). When in water, it is expected to quickly volatilize to air (EPA 1994c). Oceans, in particular, are known to be a significant source of carbonyl sulfide to the atmosphere, with emissions calculated as approximately 8×10^{11} gm/year (800,000 metric tons/year) (Meinrat et al. 1992; Rasmussen et al. 1982a).

6.2.3 Soil

Hydrogen Sulfide. Estimated releases of 374,818 pounds (~170 metric tons) of hydrogen sulfide to soils from 516 domestic manufacturing and processing facilities in 2014, accounted for about 1% of the estimated total environmental releases from facilities required to report to the TRI (TRI14 2015). These releases are summarized in Table 6-1. An additional 4.5 million pounds (~2,037 metric tons) of hydrogen sulfide were injected underground representing approximately 17% of the estimated total environmental releases from facilities required to report to the TRI (TRI14 2015).

Hydrogen sulfide may enter the soil through deposition from the atmosphere, migration of mobilized pore water, or from leaks and spills associated with manufacture, transport, or storage. Hydrogen sulfide is readily soluble in water and would exist as bisulfide or sulfide ions. Hydrogen sulfide can also form insoluble sulfide salts with various metals (i.e., copper, zinc, nickel, and iron) that may be present in soils (Pouliquen et al. 1989).

Carbonyl Sulfide. Estimated releases of 84 pounds (~0.038 metric tons) of carbonyl sulfide to soils from 136 domestic manufacturing and processing facilities in 2014, accounted for <1% of the estimated total environmental releases from facilities required to report to the TRI (TRI14 2015). These releases are summarized in Table 6-2. An additional 5 pounds of carbonyl sulfide were injected underground (TRI14 2015).

Like hydrogen sulfide, carbonyl sulfide may enter soil through atmospheric deposition. It does not bind well to soils and may be transported to groundwater. Carbonyl sulfide is typically released to air from both moist and dry soils (EPA 1994c). There is some discrepancy, however, amongst the literature as to whether soil is a source or a sink of carbonyl sulfide (Simmons et al. 2012). Previous studies labeled soil as a source of carbonyl sulfide to the atmosphere, as noted by Liu et al. (2007) and Simmons et al. (2012). However, more recent sources indicate the converse, that soil is a significant sink of atmospheric carbonyl sulfide (Kato et al. 2008; Liu et al. 2007, 2010; Simmons et al. 2012; Stimler et al. 2010). In particular, oxic soils are known to be a carbonyl sulfide sink (Liu et al. 2007, 2010). There is evidence that indicates that soils may be both sources and sinks of carbonyl sulfide (Conrad and Meuser 2000).

Simmons et al. (2012) found that soils (both with and without vegetation) were carbonyl sulfide sinks. Consumption rates varied between 3.6 and 77.7 nmol/m^2-hour; both vegetation and microorganisms contributed to the uptake of carbonyl sulfide. When areas were treated with nitrogen or lime, the carbonyl sulfide consumption was increased by 30% over the control. A clear cut site took up 3.5 times more carbonyl sulfide than the control, whereas vegetated and water-saturated soils consumed carbonyl sulfide at 43 and 84% higher rates than the non-vegetated and unsaturated soils, respectively (Simmons et al. 2012).

Release of carbonyl sulfide from soils to the atmosphere is influenced by the type of soil as well as soil temperature and water content (Liu et al. 2010). Liu et al. (2007) studied the exchange of carbonyl sulfide between lawn soil and the atmosphere. The uptake of carbonyl sulfide by lawn soil was correlated to temperature; it increased with temperature up to 298°K, and then decreased at higher temperatures. Water content also affected uptake rates, which increased with increasing water content to a maximum of 12.5% and then decreased at higher water levels. The authors concluded that due to the nonlinear relationships of carbonyl sulfide uptake with temperature and water content, carbonyl sulfide content in soil is likely controlled by biological processes. In an experiment, approximately half of the carbonyl sulfide was transformed to water-soluble sulfates by way of hydrogen sulfide (Liu et al. 2007).

Carbonyl sulfide release to the atmosphere from the soil of a temperate spruce forest in the Solling Mountains of Germany was examined in 1999 (Steinbacher et al. 2004). The results indicated a net flux of carbonyl sulfide into the soil from the atmosphere. Uptake rates of the soil were found to be 0.81 pmol/m^2-second on average, with a range of 0.23–1.38 pmol/m^2-second. The authors indicated that the carbonyl sulfide flux was slightly dependent on soil temperature and water content.

Carbonyl sulfide exchange rates were determined in soils from a forest and former rape (*Brassica napus*) field in Germany. When carbonyl sulfide concentrations exceeded 5,000 ppt in the rape field, the uptake rate constant decreased, indicating carbonyl sulfide saturation. When concentrations exceeded 50,000 ppt, the uptake rate constant increased, to which the authors attributed to a second consumption source of carbonyl sulfide. A similar process was found for the forest soil, where the uptake of carbonyl sulfide increased when concentrations were >4,000 ppt. When carbonyl sulfide concentrations were below the compensation concentrations of 785 and 1,470 ppt for the forest and rape field soils, respectively, the soil was considered a source of carbonyl sulfide to the atmosphere (Conrad and Meuser 2000).

6.3 ENVIRONMENTAL FATE

6.3.1 Transport and Partitioning

Hydrogen Sulfide. Since hydrogen sulfide exists as a gas at atmospheric pressure, partitioning to the air is likely to occur after environmental releases. However, the compound is also soluble in oil and water, and may therefore also partition to surface water, groundwater, or moist soil. In addition, sorption of hydrogen sulfide from air onto soil (Cihacek and Bremner 1993) and plant foliage (De Kok et al. 1983, 1988, 1991) occurs. Hydrogen sulfide's solubility in pure water varies with temperature from 5.3 g/L at 10°C to 3.2 g/L at 30°C (O'Neil et al. 2001). Once hydrogen sulfide is dissolved in water, it will dissociate into bisulfide ion (HS^-) and sulfide ion (S^{2-}); the ratio of the concentrations of these various ions will depend on the pH of the solution. Hydrogen sulfide can also form insoluble sulfide salts with various metals (i.e., copper, zinc, nickel, and iron) that may be present in soils or environmental waters (Pouliquen et al. 1989).

Hydrogen sulfide evaporates easily from water, and the rate of evaporation depends on factors such as temperature, humidity, pKa, pH, and the concentration of certain metal ions. Hydrogen sulfide will cross the air-water interface with kinetics similar to other unreactive gases (such as oxygen [O_2], nitrogen [N_2], and carbon dioxide [CO_2]) at pH ≤6. At higher pH (such as seawater, which has a pH of ≥8) hydrogen sulfide escape is enhanced due to an ionic species gradient in the water close to the surface (Balls and Liss 1983). The Henry's law constant was determined under a variety of conditions for hydrogen sulfide dissolved in sewage or distilled water and was found to increase linearly with temperature, indicating an increasing tendency to partition to the gas phase (Al-Haddad et al. 1989; also see Table 4-2). Other factors found to affect the Henry's law constant in sewage were pH, pK, flow rate, and initial hydrogen sulfide concentration. Complexation of bisulfide and sulfide ions to trace metal ions (i.e., Zn^{2+}, Co^{2+}, and

Ni^{2+}) found in seawater will also have an effect on the transport of hydrogen sulfide across the air-water interface (Elliott and Rowland 1990).

Clay or organic matter may sorb hydrogen sulfide. Smith et al. (1973) determined the sorption of hydrogen sulfide to six air-dried and moist soils in a laboratory study. The capacities of soil samples to sorb hydrogen sulfide ranged from 15.4 to 65.2 mg/g soil for the air-dried soils and from 11.0 to 62.5 mg/g soil for the moist soils (50% water-holding capacity). Capacities and rates of sorption were not significantly affected by sterilization of the soil sample, indicating that soil microorganisms are not likely to be involved in the sorption process. The authors noted that these values, however, would not provide reliable estimates of the amounts of hydrogen sulfide that could be sorbed by soils under natural conditions, where the environmental fate of the sorbed hydrogen sulfide would have to be considered. Under natural conditions, it is likely that some of the hydrogen sulfide would be oxidized to sulfate, which may be removed by leaching or taken up by plants. This, in turn, may make gas sorption sites available for additional sorption (Smith et al. 1973). Cihacek and Bremner (1993) showed that soils can sorb considerable amounts of hydrogen sulfide from the air, retaining it as elemental sulfur. Several species of soil, aquatic, and marine microorganisms oxidize hydrogen sulfide to elemental sulfur; its half-time in these environments usually ranges from 1 hour to several hours (Jørgensen 1982). Food chain bioconcentration and biomagnification are unlikely.

Carbonyl Sulfide. Carbonyl sulfide is a significant, non-volcanic source of sulfur in the upper atmosphere due to its long residence time and significant abundance in the troposphere (Blake et al. 2004; Simmons et al. 2012). Carbonyl sulfide can be removed from the atmosphere by terrestrial vegetation, soils, photolysis, and reaction with hydroxyl and oxygen radicals (all of which are considered to be major sinks of carbonyl sulfide) (Blake et al. 2004; Stimler et al. 2010).

Carbonyl sulfide does not adsorb to soils, particularly those rich in organic material, and thus, it may enter groundwater. It is expected to volatilize rapidly from water and both dry and moist soil, and water may leach carbonyl sulfide from soils. When released to water, it will quickly dissipate to air (EPA 1994d; Meinrat et al. 1992). Bioconcentration of carbonyl sulfide is not expected in fish or other aquatic organisms, based on an estimated bioconcentration factor ranging from 2 to 11 (EPA 1994c, 1994d).

6.3.2 Transformation and Degradation

6.3.2.1 Air

Hydrogen Sulfide. In the atmosphere, hydrogen sulfide may be oxidized by oxygen (O_2) and ozone (O_3) to give sulfur dioxide (SO_2), and ultimately sulfate compounds. Sulfur dioxide and sulfates are eventually removed from the atmosphere through absorption by plants, deposition on and sorption by soils, or through precipitation (Hill 1973). A residence time of approximately 1.7 days at an ozone concentration of 0.05 mg/m^3 has been calculated for hydrogen sulfide (WHO 1981). The effective lifetimes for hydrogen sulfide based on summer daytime and yearly average hydroxyl radical concentrations have been estimated to be 0.23 and 2.3 days, respectively, based a measured rate constant of 4.8×10^{-12} cm^3/molecule second (Cox 1975). Lifetimes in air ranging from approximately 1 day in the summer to 42 days in the winter have been estimated for hydrogen sulfide (Bottenheim and Strausz 1980). Hydrogen sulfide is not expected to be decomposed by direct absorption of ultraviolet radiation and its reaction with ozone is not expected to be a significant environmental fate (Cox 1975).

Carbonyl Sulfide. Carbonyl sulfide is considered to be fairly inert in the troposphere (Liu et al. 2007) and thus has the longest lifetime of an atmospheric sulfur species (Meinrat et al. 1992). It can undergo photolysis and reaction with hydroxyl and oxygen radicals, although both processes have been found to be very slow, or may not occur at all, in the troposphere (Blake et al. 2004; EPA 1994d; Stimler et al. 2010). The lifetime of carbonyl sulfide in the troposphere has been reported as >1 year with a range of 2–10 years (Blake et al. 2004; EPA 1994d; Liu et al. 2007; Meinrat et al. 1992; Stimler et al. 2010).

Due to its long residence time in the troposphere, carbonyl sulfide transports into the stratosphere, where photolysis and reaction with oxygen as well as photochemically-produced hydroxyl radicals is thought to be a major route of atmospheric degradation (EPA 1994d; Meinrat et al. 1992; Stimler et al. 2010). A stratospheric aerosol is formed as a result of these processes which generates a sulfate aerosol layer in the stratosphere that remains present even in the absence of volcanic activity (Conrad and Meuser 2000; Liu et al. 2007; Meinrat et al. 1992; Simmons et al. 2012; Stimler et al. 2010). The sulfate aerosol layer can affect the radiation budget of the earth and may result in increased depletion of the stratospheric ozone layer (Conrad and Meuser 2000; Liu et al. 2007; Meinrat et al. 1992; Simmons et al. 2012). Additionally, carbonyl sulfide is oxidized to sulfur dioxide in the troposphere and/or the stratosphere (which may also have an impact on climate change) (Blake et al. 2004). Carbonyl sulfide can be also removed from the atmosphere by uptake in terrestrial vegetation and soils (Blake et al. 2004; EPA 1994d; Stimler et al. 2010).

6.3.2.2 Water

Hydrogen Sulfide. In aqueous solution, hydrogen sulfide is a weak acid, exhibiting two acid dissociation constants. The first dissociation yields bisulfide ion (HS^-) and the second yields sulfide ion (S^{2-}); the pK_a values for each of these dissociations of 7.04 and 11.96, respectively (O'Neil et al. 2001). At a pH of 7.0, the ratio of the concentration of aqueous hydrogen sulfide to bisulfate ion is approximately 1-to-1. As the pH increases above 7.0, the ratio of the concentration of bisulfide ion to aqueous hydrogen sulfide increases. At a pH of 8, the ratio of the concentration of bisulfide ion to the concentration of aqueous hydrogen sulfide is approximately 10-to-1. The relative concentration of sulfide ion does not begin to increase until a pH of 11 is exceeded; only above pH 12 will the concentration of sulfide ion become significant (>50%).

Hydrogen sulfide oxidation by O_2 readily occurs in surface waters. At 25°C and pH 8, half-times of 50 and 26 hours were reported for hydrogen sulfide in water and seawater, respectively. Above pH 8, however, the rate of oxidation was independent of pH (Millero et al. 1987). Using a hydrogen peroxide concentration of 1×10^{-7} M as found in surface seawater, the half-time for sulfide oxidation by peroxide in seawater would be 2,800 hours. Only at hydrogen peroxide concentrations $>10^{-5}$ M (such as found in rainwaters) would the oxidation of hydrogen sulfide by hydrogen peroxide become competitive with the oxidation by oxygen (Millero et al. 1989). Hydrogen sulfide in waste water may be controlled by addition of oxidizing chemicals, which react to form less toxic byproducts (Tomar and Abdullah 1994). In warm, damp environments (such as manholes and gravity sewers), hydrogen sulfide may be oxidized by autotrophic bacteria to sulfuric acid (Boon 1992). Chemical oxidation of hydrogen sulfide dissolved in sewage water produces sulfur at pH 6–7, while sulfur, polysulfides, thiosulfates, and ultimately sulfate are formed at pH 7–9 (Boon 1992).

Carbonyl Sulfide. Carbonyl sulfide is rapidly removed from water through volatilization. Volatilization of carbonyl sulfide from a model river was found to have an estimated half-life of 2.3 hours (EPA 1994d). As it can dissolve in water and does not adsorb well to soils, sediments, or suspended organic matter, carbonyl sulfide may migrate to groundwater (EPA 1994c, 1994d).

Carbonyl sulfide was found to hydrolyze slowly in water, where it forms hydrogen sulfide and carbon dioxide (EPA 1994c, 1994d; PERC 2001). In the presence of water, carbonyl sulfide is corrosive to metals (Weil and Sandler 1997).

6.3.2.3 Sediment and Soil

Hydrogen Sulfide. Hydrogen sulfide is one of the principal components in the natural sulfur cycle. Bacteria, fungi, and actinomycetes (fungus-like bacteria) release hydrogen sulfide during the decomposition of sulfur containing proteins and by the direct reduction of sulfate (SO_4^{2-}). Hydrogen sulfide is also consumed by bacteria found in soil and water that oxidize hydrogen sulfide to elemental sulfur. Photosynthetic bacteria can oxidize hydrogen sulfide to sulfur and sulfate in the presence of light and the absence of oxygen (EPA 1993; WHO 1981). A number of microorganisms have been found to degrade hydrogen sulfide to elemental sulfur or sulfate. Among these are a heterotrophic bacterium of the genus *Xanthomonas* isolated from dimethyl disulfide-acclimated peat (Cho et al. 1992), heterotrophic fungi (Phae and Shoda 1991), and a marine isopod (Vismann 1991). Soils may sorb considerable amounts of hydrogen sulfide from the air, retaining most of it in the form of elemental sulfur. Manganese compound found in these soils appeared to catalyze the oxidation of hydrogen sulfide to elemental sulfur (Cihacek and Bremner 1993).

Carbonyl Sulfide. Carbonyl sulfide does not adsorb to soils and sediments and will volatilize rapidly from both dry and moist soil. It is highly mobile in soil and may be transported out of soil by water (EPA 1994c, 1994d).

Carbonyl sulfide has been found to degrade in soil (Kato et al. 2008). A study by Kato et al. (2008) found that *Mycobacterium* spp. in soil degraded ambient carbonyl sulfide. One strain (THI401) degraded 30 ppm by volume of carbonyl sulfide in 1 hour, decreasing 60% of the initial amount by abiotic conversion in 30 hours. Testing was performed at an ambient carbonyl sulfide concentration of 500 ppt in sterilized soil samples. While it was emitted from the soil during testing, the *Mycobacterium* spp. was found to degrade the carbonyl sulfide more quickly than it was emitted (Kato et al. 2008).

6.3.2.4 Other Media

Carbonyl Sulfide. Uptake of carbonyl sulfide by various biological organisms may be driven by carbonic anhydrase, which is a key enzyme that splits carbonyl sulfide *in vivo* into carbon dioxide and hydrogen sulfide (Liu et al. 2007).

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to hydrogen sulfide and carbonyl sulfide depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of hydrogen sulfide and carbonyl sulfide in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on hydrogen sulfide and carbonyl sulfide levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable. The analytical methods available for monitoring hydrogen sulfide and carbonyl sulfide in a variety of environmental media are detailed in Chapter 7.

6.4.1 Air

Hydrogen Sulfide. The concentration of hydrogen sulfide in air can be represented using various concentration units. All air monitoring data reported herein are reported in or have been converted into ppm or ppb for ease of comparison. The conversion factors are: 1 ppm=1.40 mg/m^3 and 1 ppb=1.40 μg/m^3.

Hydrogen sulfide ambient air concentrations from natural sources have been estimated to be between 0.11 and 0.33 ppb (EPA 1993). In an unpolluted area of Colorado, concentrations between 0.02 and 0.07 ppb were measured (Hill 1973). Near ground level, samples taken around a sulfurous New Zealand lake charged by an active underground geothermal vent had average hydrogen sulfide levels in the range of 0.125–3.9 ppm, which produced no visible adverse effects on indigenous bird or plant populations (Siegel et al. 1986). Hydrogen sulfide concentrations in air in remote marine environments are reported to be highly variable, ranging from 0.001 to 0.1 ppb (Elliott and Rowland 1990). Concentrations of hydrogen sulfide in urban areas are generally <1 ppb (Svendsen 2001). Hydrogen sulfide concentrations >90 ppb were measured during several intermittent periods in the Conimicut Point neighborhood in Warwick, Rhode Island that resulted from rotting seaweed and shellfish from a "die-off" of aquatic plants and animals that occurred in August 2003 in parts of the eastern Narragansett Bay. The concentration of hydrogen sulfide in the residential areas varied over time, depending on the tides, winds, and weather (Fulton et al. 2003).

Indoor air was monitored in five residential homes in the Dakota City/South Sioux City area in Nebraska from April 2 to May 15, 1997. Hydrogen sulfide was routinely found in the indoor air of these homes. In general, hydrogen sulfide was found to not exceed 90 ppb (which was the upper detection limit for the measuring device used in this monitoring study). However, at one home, hydrogen sulfide was found to exceed the upper detection limit for periods of 20 minutes to >3 hours on 10 of the 30 days of sampling (ATSDR 1997).

Durand and Scott (2005) monitored nine properties in the Rotorua geothermal field area in New Zealand for various geothermal gases, including hydrogen sulfide. These buildings or the site had a history of geothermal gases penetrating to the inside of the buildings. All buildings in this study were found to have chronic contamination of the indoor air by hydrogen sulfide, with the entry of the gas through cracks in floors and subsurface ducts as the most common means of entry. The highest levels of hydrogen sulfide were reported to be emitted from a vent in a concrete floor of a residential property at 435 ppm. In another location, two interior hydrogen sulfide vents were found, with one vent containing hydrogen sulfide at >200 ppm and the other at 2.9–4.1 ppm (Durand and Scott 2005).

In early 1999, ATSDR and EPA conducted a 12-month hydrogen sulfide monitoring program in Dakota City. Sixteen hydrogen sulfide monitors were stationed in selected locations around the Dakota City area. White et al. (1999) noted that the frequency and concentration of hydrogen sulfide levels in Dakota City were higher than in a typical urban setting. During 6 months in 1999, peak hydrogen sulfide concentrations >90 ppb (the upper detection limit) were recorded at four monitoring locations, and three of these locations had multiple peak concentrations exceeding 90 ppb. Multiple peak levels in the range of 30–50 ppb were recorded for other residential areas. For three monitoring locations that were distant from a known source of hydrogen sulfide, peak levels of 9 and 19 ppb were recorded while most measurements were below the detection limit of 2 ppb (White et al. 1999).

An air monitoring study at a waste water treatment plant in Australia found time-averaged hydrogen sulfide levels of 1–2 ppm near the primary clarifiers and inlet structure, and levels <1 ppm at various other locations in the 10-hectare plant site (Koe 1985). Hydrogen sulfide was not detected by air-sampling instruments located around the perimeter of a landfill in Ohio after a major landslide occurred in March 1996 (Ingram et al. 1997). In a study to determine the quantity and composition of reduced sulfur gases (including hydrogen sulfide) being released to the atmosphere at waste water treatment plants in Baton Rouge, Louisiana at various steps of the treatment process, hydrogen sulfide was found to be the dominant sulfur compound emitted. The concentrations of hydrogen sulfide were typically <7.5 ppm sulfur, with concentrations ranging from 0.013 ppm sulfur (central treatment plant final effluent box) up to 340 ppm sulfur (central treatment plant digester dome of the floating roof) (Devai and DeLaune 1999). The hydrogen sulfide concentration in the atmosphere of a Norwegian sewage purification plant was generally below 2 ppm; however, a peak concentration of 100 ppm was detected (Søstrand et al. 2000). As part of the 1997 Fresh Kills Air Monitoring Program, >140,000 observations of ambient air were collected over a 2-month period at 16 locations on Staten Island, New York. Hydrogen sulfide was measured at detectable levels in only about half of the samples, with measured levels ranging from 2 ppb (the detection limit) to 33 ppb (ATSDR 2000).

Hydrogen sulfide concentrations in air can vary widely during manure management activities. Levels of hydrogen sulfide in air in pig barns during normal operations are generally <5 ppm. However, concentrations can rapidly rise up to 800 ppm inside manure transfer pits or lift stations when the manure is agitated; additionally, the hydrogen sulfide can back up into pig rooms through open pits or piping. Concentrations of hydrogen sulfide have been shown to increase from very low levels to 1,300 ppm in deep-pit buildings when manure is agitated (Chénard et al. 2003).

The concentrations of sulfur compounds (including hydrogen sulfide) were measured in the air at four paper pulp mills using the kraft (sulfate) process. In this process, steam, high temperature, high pressure, and a solution containing sodium hydroxide and sodium sulfide are used to digest wood chips. Various sulfur gases are produced during this process. Hydrogen sulfide concentrations ranged from not detected (<0.2 ppm) to 35 ppm at various emission sources in the continuous digester, batch digester, and pulp washing areas. In general, hydrogen sulfide was not detected in ambient air sampled at these plants (Goyer 1990). A survey of occupational exposure in nonproduction departments of pulp, paper, and paper product mills from 147 mills in 11 countries found that hydrogen sulfide was below the detection limit in 45% of the 20 measurements taken at 6 mills. A mean concentration of 2.9 ppm was reported, with a maximum value of 53 ppm and a lowest detected value of 0.04 ppm (Teschke et al. 1999). The concentrations of various pollutants were measured in the air of five textile factories (which included three weaving and dyeing factories and two clothing factories); hydrogen sulfide concentrations ranged from <0.007 to 1.32 ppm (Rimatori et al. 1996).

Ten air samples were collected for hydrogen sulfide at the World Trade Center disaster site in New York City between September 18 and October 4, 2001. Concentrations ranged from not detected (3 of the 10 samples) to 3.0 ppm (Wallingford and Snyder 2001).

Some U.S. homes built between 2001 and 2008 contain imported drywall, also known as “Chinese drywall or problem drywall”. The U.S. Consumer Product Safety Commission conducted an emission and corrosion study of 51 homes. Indoor air concentrations of hydrogen sulfide were significantly higher in homes reporting drywall-related complaints with a mean concentration of 0.66 ppb (0.19–2.33 ppb) compared with a mean concentration 0f 0.45 ppb (0.2–2.23 ppb) in non-complaint homes (CPSC 2010a).

The Air Quality System (AQS) database is EPA's repository of criteria air pollutant and hazardous air pollutants monitoring data. Detailed air monitoring data for carbonyl sulfide was not located; however, data were reported for hydrogen sulfide. Table 6-4 illustrates the annual mean percentile distributions of hydrogen sulfide from monitoring sites in the United States for years 2010–2015. Data for previous years and other pollutants may also be obtained from the AQS website; however, no data for carbonyl sulfide were located in the AQS.

Carbonyl Sulfide. Carbonyl sulfide is the most prevalent, longest-lived sulfur-containing gas in the troposphere (Blake et al. 2004; Conrad and Meuser 2000; Meinrat et al. 1992; Stimler et al. 2010). Global mean concentrations in the troposphere have been reported as 500–510 ppt (Blake et al. 2004; Conrad and Meuser 2000; Meinrat et al. 1992).

Carbonyl sulfide concentrations in the ambient air were reported for several urban and rural areas in the United States. Air concentrations in the rural areas ranged from 0.11 to 0.33 ppb. Concentrations of carbonyl sulfide in air from urban areas were as follows: 0.18 ppb (Philadelphia, Pennsylvania); 0.496 ppb (Wallops Island, Virginia); and 0.56 ppb (Lawton, Oklahoma). Carbonyl sulfide air concentrations over salt marshes (one of the main natural sources of carbonyl sulfide) ranged from approximately 25 to 740 ppb, while air samples from over the ocean ranged from 5.7 to 7.8 ppb (EPA 1994d).

Carbonyl sulfide concentrations in air were measured over the western pacific and Asia in the spring of 2001. Concentrations over the western Pacific were found to decrease 10% from the surface to 8–10 km in altitude. It was thought that terrestrial carbonyl sources dominated the output during the springtime of that year. A mean carbonyl sulfide concentration of 580 ppt was measured below 2 km in altitude near the coast of Asia, which coincided with the area where air from urban Asia had the most impact (Blake et al. 2004).

Rasmussen et al. (1982a) collected air samples in both the North Atlantic and Pacific oceans. The concentrations of carbonyl sulfide from the samples were nearly uniform, and thus, an average value of 472±86 ppt was reported (Rasmussen et al. 1982a).

Table 6-4. Percentile Distribution of Annual Mean Hydrogen Sulfide Concentrations (ppm) Measured in Ambient Air at Locations Across the United States

Year	Number of U.S. locations	25th	50th	75th	95th	Maximum
2010	22	0.00084	0.0010	0.0013	0.0036	0.0038
2011	21	0.00078	0.0010	0.0013	0.0034	0.0057
2012	22	0.00086	0.00010	0.0012	0.0026	0.0063
2013	23	0.0010	0.0010	0.0011	0.0025	0.0056
2014	23	0.00076	0.0010	0.0012	0.0023	0.0052
2015[a]	14	0.00073	0.00099	0.0010	0.0026	0.0028

[a] Data from January 1, 2015 to June 20, 2015.

Source: EPA 2015b

6.4.2 Water

Hydrogen Sulfide. Hydrogen sulfide readily evaporates from surface waters and is not likely to persist in highly oxygenated waters; levels in these environments are expected to be low. Groundwater samples from an area receiving acid-mine drainage in Colorado averaged 0.9 ppm of hydrogen sulfide, while samples from a power plant site averaged 0.03 ppm (Patterson and Runnells 1992).

Accurate measurements of hydrogen sulfide water levels are usually complicated by the presence of other sulfide compounds. At pH ≥7, hydrogen sulfide is significantly dissociated, and the exact source of sulfide would not necessarily be known. A method of determining sulfide concentration in unspecified waste water by first transforming it to hydrogen sulfide and then measuring the atomic absorption of the product yielded results ranging from 3.1 to 5.1 ppm of sulfide sulfur (Parvinen and Lajunen 1994). Total sulfide levels in samples from the Mississippi River were about 0.92 ppm, while levels in pond and well water in St. Paul, Minnesota were 1.6 and 1.9 ppm, respectively (Slooff et al. 1991).

Nearshore hydrogen sulfide eruptions occur in the Atlantic Ocean along the central coast of Nambia. Dissolved hydrogen sulfide concentrations were found to range from <0.02 to 3.39 ppm in water sampled at various depths during eruption events that occurred during 2001–2002 (Weeks et al. 2004).

Carbonyl Sulfide. Surface water samples from temperate and subtropical North Atlantic regions and the Gulf of Mexico were found to be supersaturated with carbonyl sulfide with respect to atmospheric equilibrium. Carbonyl sulfate concentrations followed a diel pattern. The highest concentrations were measured in coastal and shelf water samples. Concentrations of carbonyl sulfide were determined for various biogeographic regions, including oligotrophic, transition, upwelling, and coastal/shelf as 13, 24, 27, and 112 pmol/L, respectively. Fluxes for the same regions were calculated as 0.9, 1.6, 2.3, and 7.9 Gmol/L, respectively. The total carbonyl sulfide concentration from the study was determined to be 32 pmol/L. The total flux of carbonyl sulfide to the atmosphere from the oceans was estimated to be 12.7 Gmol/year (0.41 Tg sulfur/year). The authors found that the concentration as well as the flux of carbonyl sulfide between the ocean and the atmosphere was highly dependent on marine productivity (Meinrat et al. 1992).

Carbonyl sulfide has also been identified in waste water at treatment plants. Carbonyl sulfide, along with hydrogen sulfide and methyl mercaptans, are responsible for the odors that emanate from such facilities (Sattler and Rosenberk 2006).

6.4.3 Sediment and Soil

Hydrogen Sulfide. Hydrogen sulfide levels as high as 11.7 ppm in soil water were measured in Louisiana rice fields (Hollis 1985). The hydrogen sulfide in these samples was presumably bound to colloidal clay or organic matter, as these levels were higher than typical solubility would predict and were not accompanied by the characteristic hydrogen sulfide odor. Sediment pore water from the Grand Calumet River in an industrialized area of Indiana contained 0.2–1.5 ppb of hydrogen sulfide (Hoke et al. 1993). In general, undisturbed anoxic sediment pore water may contain up to 100 ppb hydrogen sulfide, while disturbed sediments typically contain pore water concentrations of 1–30 ppb (Dillon et al. 1993).

Carbonyl Sulfide. Carbonyl sulfide concentrations in soil from a forested area and a former rape (*B. napus*) field were found to range from 250 to 120,000 ppt (Conrad and Meuser 2000).

6.4.4 Other Environmental Media

Hydrogen Sulfide. Hydrogen sulfide is commonly found in coal, petroleum, and natural gas deposits and may be mobilized by human manipulation of these resources. Coal gasification (a process whereby coal is subjected to heat and steam treatment to produce a convenient energy source) results in a gas product consisting of up to 1% hydrogen sulfide (Barik et al. 1987). Hydrogen sulfide was identified as a component in the vapor phase of cigarette smoke (Dong et al. 2000), and was found in the emissions of gasoline vehicles (Collier et al. 2002).

Hydrogen sulfide formation has been demonstrated in pediatric intravenous amino acid solutions used to treat infants with high protein requirements (Decsi and Koletzko 1993). Levels up to 1.96 ppm were found, presumably formed by sulfide liberation from cysteine derivatives during heat sterilization. Similar chemical reactions may explain the presence of hydrogen sulfide in dental plaque (Tonzetich and Carpenter 1971). Meat products may be contaminated with hydrogen sulfide-producing bacteria, resulting in off-odors and spoilage (McMeekin and Patterson 1975).

Hydrogen sulfide is produced in the large intestine of mammals by metabolism of sulfhydryl proteins by anaerobic bacteria, and may compose up to 10% of intestinal gases (Beauchamp et al. 1984; EPA 1978). Hydrogen sulfide was found in the gas produced by feces of infants; levels were found to vary based on the types of diets the infants were fed and the age of the infants. Fecal gas production for infants aged 1–3 months was 372–833, 73–371, and 1,904–2,540 nmol/g (12.7–28.3, 2.5–12.6, and 65.8–86.4 μg/g) dry weight for infants fed breast milk, milk-based formula, and soy based formula, respectively (Jiang et al. 2001). Fecal sulfide concentrations in 15 adult volunteers ranged from 110 to 720 nmol/g (3.74–24.5 μg/g) wet weight. Fecal sulfide concentrations were found to increase significantly from 160 to 750 nmol/g (5.4–26 μg/g) when subjects were fed diets containing increasing amounts of meat. Sulfide concentrations in whole-blood samples from six healthy adults were found to range from 10 to 100 μmol/L (0.3–3 μg/mL). When increasing amounts of protein from meat were added to the diet of these subjects, blood sulfide concentrations did not change significantly (Richardson et al. 2000). Hydrogen sulfide is also produced in the human mouth by microbial putrefaction (Rosenberg et al. 1991). Mean sulfide levels in human brainstem controls were reported as 0.69 and 0.59 μg/g for males (n=36) and females (n=9), respectively. Sulfide concentrations of 0.91 and 1.04 μg/g were reported in brainstems from two suspected hydrogen sulfide inhalation fatalities (Goodwin et al. 1989). Concentrations of sulfide in the blood, brain, lung, and femoral muscle of a victim of a fatal hydrogen sulfide poisoning were 0.45 μg/mL, 2.72 μg/g, 0.42 μg/g, and 0.16 μg/g, respectively. The victim was kept at 0°C until autopsy, 20 hours after death; these conditions were expected to significantly suppress sulfide production due to putrefaction (Kage et al. 1998). Blood sulfide levels at 4 μg/mL were found in an individual who died while working at a treatment, storage, and disposal facility for hazardous waste materials. Sulfide levels were also analyzed in tissue samples and confirmed that the blood sulfide concentrations could not be attributed to cellular decay. Through an investigation by OSHA, it was determined that high concentrations of hydrogen sulfide were apparently generated during the waste acid neutralization process (Smith and Cummins 2004).

Hydrogen sulfide was detected in emission testing of drywall samples. In the 30 samples, hydrogen sulfide emissions ranged from not detected to 200.60 μg-S/m^2/hour) (CPSC 2010b).

Carbonyl Sulfide. Emission tests of drywall samples have detected a number of reactive sulfur compounds, including hydrogen sulfide and carbonyl sulfide. The levels of carbonyl sulfide in the 30 drywall samples tested ranged from not detected to 4.25 μg-S/m^2/hour (CPSC 2010b).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Hydrogen Sulfide. Primary exposure of the general population to hydrogen sulfide most likely occurs through inhalation of ambient air. As hydrogen sulfide is part of the natural environment, the general population will have some exposure to hydrogen sulfide. Hydrogen sulfide is produced in the human large intestine by the bacterial reduction of inorganic sulfate and sulfite, and by fermentation of sulfur-containing amino acids, cysteine, and methionine (Richardson et al. 2000); it can compose up to 10% of intestinal gases (EPA 1978). Hydrogen sulfide is produced by the natural bacteria found in the human mouth, and is a component of bad breath (halitosis) (Rosenberg et al. 1991).

Hydrogen sulfide may occur naturally in well water, and can be formed in hot water heaters, giving household hot tap water an unpleasant odor. Formation of hydrogen sulfide can occur by the reduction of sulfates in the water by sulfur bacteria (which can thrive in the warm environment of the hot water heater) or by reaction with the magnesium anode in the hot water heater tank (MDH 2004). Populations living in areas of geothermal activity, near waste sites or industries such as petroleum refineries, natural gas plants, petrochemical plants, coke oven plants, kraft paper mills, food processing plants, landfills, manure treatment facilities, waste water treatment facilities, and tanneries may be more likely to be exposed to higher levels of hydrogen sulfide. Geothermal gases (including hydrogen sulfide) were found to be entering buildings in Rotorua, New Zealand directly from the ground through floors, walls and subsurface pipes; indoor vents emitting up to approximately 200 ppm were reported (Durand and Scott 2005). The general population may also be exposed to hydrogen sulfide by accidental release ("blowout") from natural gas wells during drilling operations near residential areas (Layton and Cederwall 1986; Leahey and Schroeder 1986). Exposures to hydrogen sulfide have occurred through the mixing of acid and basic drain cleaners and through the use of acid drain cleaner to remove sludge-clogged drains, but these incidents are thought to be rare (Oderda 1975).

Residents of the Conimicut Point neighborhood in Warwick, Rhode Island were exposed to hydrogen sulfide from rotting seaweed and shellfish caused by a "die-off" of aquatic plants and animals that occurred on August 20, 2003 in parts of the eastern Narragansett Bay. The concentration of hydrogen sulfide in the residential areas varied over time, depending on the tides, winds, and weather. During the week of September 15, 2003, the Rhode Island Department of Environmental Management measured several intermittent periods when hydrogen sulfide concentrations were >90 ppb (Fulton et al. 2003). Emissions from the Fresh Kills Landfill on Staten Island, New York, which contain hydrogen sulfide, are blown by prevailing winds into nearby neighborhoods (ATSDR 2000).

Workers may be occupationally exposed to hydrogen sulfide from fermenting manure (Chénard et al. 2003; Morse et al. 1981), stagnant wells (McDonald and McIntosh 1951), areas of waste-water treatment facilities (NIOSH 1980, 1984, 1985a, 1985c, 1990), extruded rubber plants (NIOSH 1985b), landfills (Lehman 1996), textile industries (Rimatori et al. 1996), and petroleum refineries (NIOSH 1982a, 1982b). Facilities where hydrogen sulfide can be generated include petroleum refineries, natural gas plants, petrochemical plants, coke oven plants, kraft paper mills, viscose rayon manufacturing plants, sulfur production facilities, iron smelters, food processing plants, and tanneries (Svendsen 2001). Major occupational exposures to hydrogen sulfide have resulted from its presence as a byproduct of chemical reactions that may take place in viscose rayon and leather tanning processes (ACGIH 1991). Hydrogen sulfide is also used as an agricultural disinfectant and as an additive in lubricants and cutting oils (Bingham et al. 2001; Sittig 2002). Hydrogen sulfide may also be encountered in various industrial processes including the manufacture of dyes and pigments, felt, rayon and artificial silk; in brewing, glue making, and rubber vulcanization; and in lithography and photoengraving (Beck et al. 1981; Grant and Schuman 1993; Sittig 2002). Hydrogen sulfide levels were measured using personal monitors worn by farm workers in Norway during 1992–1996 while performing various tasks, such as handling of harvest, tending to animals, and handling of manure. Hydrogen sulfide was only detectable in 7 out of 23 measurements with a range of peak values of 0.2–6 ppm (Eduard et al. 2001).

In the most recent annual report of national poison control centers (2012) compiled from 57 centers, there were 809 reports of hydrogen sulfide exposure (Mowry et al. 2013). Approximately 42% of the exposures resulted in no or minor outcomes, 12% had moderate outcomes, 1.6% had major outcomes, and there were five deaths (0.6%). The numbers of reported hydrogen sulfide exposures were higher in the 2010 (1,054 cases), 2005 (1,396 cases), 2000 (1,382 cases), and 1995 (1,407 cases) annual reports (Bronstein et al. 2011; Lai et al. 2006; Litovitz et al. 1996, 2001). The outcome severity was similar for the different reporting years, with the exception that no deaths were reported in 1995.

Carbonyl Sulfide. Exposure of the general population to carbonyl sulfide is primarily through inhalation of ambient air. Carbonyl sulfide is a component of the global sulfur cycle and exists in the atmosphere at high concentrations (Conrad and Meuser 2000; Meinrat et al. 1992; Simmons et al. 2012; Stimler et al. 2010; Wright 2000). It is released to the atmosphere from various natural and anthropogenic sources, including wetlands, soil, trees, volcanic gases, oceans, biomass burning, aluminum production, combustion of coal, extraction of gas and oil, automobiles, and chemical processing, among others (ASTM International 2012; Blake et al. 2004; EPA 1994c, 1994d; Meinrat et al. 1992; PERC 2001; Rasmussen et al. 1982a, 1982b; Stimler et al. 2010). Due to these numerous sources, there is constant exposure to low levels of carbonyl sulfide (Wright 2000). The frequency and duration of exposure influences the effect carbonyl sulfide has on human health (EPA 1994c).

Carbonyl sulfide may be used as a fumigant for commodities and structures, which could potentially result in exposure to the general population. Wheat, oats, barley, and canola (which have natural, background carbonyl sulfide levels ranging from 0.05 to 0.1 mg/kg) can be treated with carbonyl sulfide to increase insect resistance. An Australian study, however, found that post fumigation carbonyl sulfide residues used in wheat, oat, barley, and canola field trials were less than the Australian maximum residue level of 0.2 mg/kg after being aired for 4 hours. Consequently, the study concluded that carbonyl sulfide is completely removed from commodities after fumigation and concentrations in grains and seeds are not discernible from levels in untreated grains. Carbonyl sulfide is rapidly desorbed after fumigation (Wright 2000). Exposure may also result from natural levels of carbonyl sulfide found in foods, such as cheese and vegetables in the cabbage family (Wright 2000).

In occupational settings, exposure to carbonyl sulfide is mainly inhalation from its production and use as a chemical intermediate (EPA 1994d), such as in the viscose rayon industry (Kamstrup and Hugod 1979). It is also a byproduct in petroleum refining and coal distillation, and thus, workers in gas production and distribution facilities may be exposed to carbonyl sulfide in higher concentrations than the general public (Khalil and Rasmussen 1984). As carbonyl sulfide targets the central nervous system and can result in narcotic effects and respiratory paralysis (Chase et al. 2010; Lewis 2007), monitoring is important to warn those in enclosed facilities of carbonyl sulfide releases (Chase et al. 2010).

6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in Section 3.7, Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume than adults. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and may spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Hydrogen Sulfide. Hydrogen sulfide is found naturally in crude petroleum, natural gas, volcanic gases, hot springs, and often as the result of bacterial breakdown of organic matter. Children may be exposed to hydrogen sulfide if they live or play near animal waste sites including places where there might be sediments of fish aquaculture, livestock barns, or manure areas. Inhalation is the most likely route of exposure, and there are no known hydrogen sulfide exposure pathways generally unique to children; hydrogen sulfide is heavier than air (which may increase their risk of exposure to higher concentrations than adults). Children living in areas of geothermal activity, near waste sites or industries such as petroleum refineries, natural gas plants, petrochemical plants, coke oven plants, kraft paper mills, food processing plants, and tanneries are more likely to be exposed to higher levels of hydrogen sulfide due to physiological and behavior factors previously mentioned. Geothermal gases (including hydrogen sulfide) were found to be entering buildings in Rotorua, New Zealand directly from the ground through floors, walls, and subsurface pipes; indoor vents emitting up to approximately 200 ppm were reported. This concentration is high enough to present an acute respiratory hazard to persons close to the vent, such as children playing on the floor (Durand and Scott 2005). In a clinical case involving a 20-month-old child whose parents lived beside a coal mine where a burning tip had been emitting hydrogen sulfide for nearly 1 year, the patient had symptoms of ataxia and an abnormal CT scan of the brain (Gaitonde et al. 1987). Monitoring data showed that the hydrogen sulfide levels in the air were approximately 0.6 ppm, but may have been higher before data were collected.

Hydrogen sulfide is also produced by bacteria in the mouth and gastrointestinal tract. Hydrogen sulfide formation has been demonstrated in pediatric intravenous amino acid solutions used to treat infants with high protein requirements (Decsi and Koletzko 1993). Levels up to 1.96 ppm were found, presumably formed by sulfide liberation from cysteine derivatives during heat sterilization.

There are no known studies in which hydrogen sulfide levels were measured in the blood or other tissues of children. Hydrogen sulfide was found in the gas produced by feces of infants, and levels were found to vary based on the types of diets the infants were fed and the age of the infants. Fecal gas production for infants aged 1–3 months were 372–833, 73–371, and 1,904–2,540 nmol/g (12.7–28.3, 2.5–12.6, and 65.8–86.4 μg/g) dry weight for infants fed breast milk, milk based formula, and soy based formula, respectively (Jiang et al. 2001).

It is not clear whether hydrogen sulfide can be transferred from mother to fetus. There is limited evidence that women occupationally exposed to hydrogen sulfide have a higher rate of spontaneous abortions. Women employed in rayon textile and paper products jobs in Finland were found to have an increased rate of spontaneous abortions when the mean annual level of hydrogen sulfide exceeded 3 ppb

(Hemminki and Niemi 1982). An increase in spontaneous abortions was also found in women working in petrochemical plants in China as compared to women working in non-chemical plants (Xu et al. 1998).

Carbonyl Sulfide. As carbonyl sulfide exists in the atmosphere due to both natural and anthropogenic sources, children can be exposed through inhalation of ambient air (Conrad and Meuser 2000; Meinrat et al. 1992; Simmons et al. 2012; Stimler et al. 2010; Wright 2000). Natural sources, such as soils and oceans, as well as human activities (including combustion of coal, automobile use, and chemical processing) can introduce carbonyl sulfide to the air (ASTM International 2012; Blake et al. 2004; EPA 1994c, 1994d; Meinrat et al. 1992; PERC 2001; Rasmussen et al. 1982a; Stimler et al. 2010). Children may therefore be exposed to a constant, low level of carbonyl sulfide (Wright 2000). The main exposure concerns are typically associated with occupational settings where carbonyl sulfide is produced and used (such as for a chemical intermediate [EPA 1994d]), and in this context, childhood exposure may be limited.

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Hydrogen Sulfide. Workers employed at facilities that manufacture or use hydrogen sulfide in the production process are especially prone to exposure. Such industries include the manufacture of rayon textiles, lubricants, pulp and paper, and sulfuric acid and inorganic sulfides. Workers in facilities where hydrogen sulfide is produced as a byproduct (such as farms with manure storage pits, petroleum or natural gas drilling operations, landfills, and waste water treatment plants) may also be exposed to high levels of hydrogen sulfide.

Carbonyl Sulfide. People in occupational settings where carbonyl sulfide is used and produced are likely to have the highest rates of exposure. In particular, workers in a facility where carbonyl sulfide is used as a chemical intermediate are particularly at risk of exposure (EPA 1994d). Those in the petroleum refining, gas production and distribution facilities, and coal distillation fields may be exposed to carbonyl sulfide in higher concentrations than the general public (EPA 1994c). Working with carbonyl sulfide in an enclosed facility increases the likelihood of exposure during a release (Chase et al. 2010).

6.8 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of hydrogen sulfide and carbonyl sulfide is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of hydrogen sulfide and carbonyl sulfide.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.8.1 Identification of Data Needs

Physical and Chemical Properties.

Hydrogen Sulfide. Information is available on the physical and chemical properties of hydrogen sulfide (Al-Haddad et al. 1989; Amoore and Hautala 1983; Daubert and Danner 1989; HSDB 2013; NIOSH 2011; O'Neil et al. 2001). However, additional information on those properties that determine the specific fate, transport, and rates of transformation of hydrogen sulfide as part of the larger sulfur cycle would be useful in discerning the environmental fate and behavior of this compound.

Carbonyl Sulfide. Physical and chemical properties of carbonyl sulfide are reasonably well characterized (EPA 1994c; HSDB 2007; Lewis 2007).

Production, Import/Export, Use, Release, and Disposal. According to the Emergency Planning and Community Right-to-Know Act of 1986 (42 U.S.C. Section 11023), industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information for 2014, became available in November of 2015. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate.

Hydrogen Sulfide. Hydrogen sulfide is known to easily evaporate into the air (EPA 1993; Layton and Cederwall 1986; Leahey and Schroeder 1986), although its solubility in water may also cause it to persist in unperturbed, anoxic sediments. Additional information on the transport, transformation, and persistence of the compound in soils and groundwater (particularly at hazardous waste sites) would be useful in identifying the most important routes of human exposure to hydrogen sulfide.

Carbonyl Sulfide. Likewise, carbonyl sulfide is typically released to air, where it is highly abundant (Conrad and Meuser 2000; Meinrat et al. 1992; Simmons et al. 2012; Stimler et al. 2010). Additional information concerning the transport, transformation, and persistence of carbonyl sulfide in soils and water would be useful.

Bioavailability from Environmental Media. Additional information on absorption following dermal contact with, or ingestion of, contaminated soil and water would also be helpful in determining the importance of these routes of exposure for populations of concern for both hydrogen sulfide and carbonyl sulfide.

Food Chain Bioaccumulation.

Hydrogen Sulfide. Sufficient information is available to demonstrate that hydrogen sulfide is not likely to bioaccumulate or biomagnify in the food chain.

Carbonyl Sulfide. While carbonyl sulfide is not expected to bioconcentrate in aquatic organisms (EPA 1994c, 1994d), additional experimental data in support of this would be useful.

Exposure Levels in Environmental Media. Reliable monitoring data for the levels of hydrogen sulfide and carbonyl sulfide in contaminated media at hazardous waste sites are needed so that the information obtained on levels of hydrogen sulfide and carbonyl sulfide in the environment can be used in combination with the known body burden of hydrogen sulfide and carbonyl sulfide to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

Hydrogen Sulfide. Monitoring of hydrogen sulfide levels in ambient air is currently sporadic; additional, more systematic sampling is needed, particularly in areas that may have a significant source of hydrogen sulfide. Methods for accurately measuring dissolved sulfides in water are also available (APHA 1998). As hydrogen sulfide is a weak acid, concentrations of aqueous hydrogen sulfide will depend on the pH of the solution. The concentration of un-ionized hydrogen sulfide can be calculated from the concentration of dissolved sulfide components, the pH of the solution, and the acidity constants for hydrogen sulfide (APHA 1998). Reliable monitoring data for the levels of hydrogen sulfide in contaminated media at hazardous waste sites are needed so that the information obtained on levels of hydrogen sulfide in the environment can be used in combination with the known body burdens of hydrogen sulfide to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites. More data on the levels of hydrogen sulfide at the point of emission (on-site) versus levels at the point of exposure (off-site) would be useful.

Carbonyl Sulfide. Likewise, while monitoring data in air exist for carbonyl sulfide, experimental data for concentrations in water and soil would be useful.

Exposure Levels in Humans.

Hydrogen Sulfide. Occupational studies often do not report exposure levels. Additional information is needed on the exposure levels among populations living in the vicinity of hazardous waste sites and other potential sources of hydrogen sulfide, such as hot springs and waste water treatment plants.

Carbonyl Sulfide. For carbonyl sulfide, exposure levels in occupational settings would be useful.

This information is necessary for assessing the need to conduct health studies on these populations.

Exposures of Children. The only information that provided an assessment of exposure of children and adolescents to hydrogen sulfide was that developed during the South Karelia Air Pollution Study in southeastern Finland where there are a cluster of pulp mills using the sulfate method (Marttila et al. 1994b); however, determining the magnitude of these exposures was complicated by the study's analysis of only gross sulfur concentrations rather than measuring the concentrations of individual sulfur-containing compounds and particulates. Additional exposure information is needed from communities where only hydrogen sulfide exceeds background levels. No exposure studies directly related to children were found for carbonyl sulfide. Additional information identifying the risks specific to children would be useful.

Child health data needs relating to susceptibility are discussed in Section 3.12.2, Identification of Data Needs: Children’s Susceptibility.

Exposure Registries. No exposure registries for hydrogen sulfide or carbonyl sulfide were located. These substances are not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. These substances will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to these substances.

6.8.2 Ongoing Studies

No ongoing studies were located for hydrogen sulfide or carbonyl sulfide.