

6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Hydrogen sulfide has been identified in at least 35 of the 1,689 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2006). However, the number of sites evaluated for hydrogen sulfide is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, all are located within the coterminous United States.

Hydrogen sulfide is one of the 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 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). Hydrogen sulfide is commonly emitted from volcanoes, stagnant or polluted waters, and manure or coal pits with low oxygen content. These natural sources account for about 90% of the total hydrogen sulfide in the atmosphere (EPA 1993). Hydrogen sulfide may also enter the environment through accidental release, from leakage during manufacture or use, or as a result of industrial waste disposal. Because hydrogen sulfide is a natural component of petroleum, sulfur, and natural gas deposits, it may also be released into the environment during the extraction, transport, and refining of these resources. Landfills are another source of ambient hydrogen sulfide in the air (HazDat 2006; Lehman 1996). Sulfides, including hydrogen sulfide, constitute up to 1% by volume of typical landfill gases (Agency for Toxic Substances and Disease Registry 2001). The Fresh Kills Landfill on Staten Island, New York has been estimated to release approximately 16 tons of hydrogen sulfide to the air annually (Agency for Toxic Substances and Disease Registry 2000). Hydrogen sulfide is frequently found in industrial settings where it is either used as a reactant or is produced as a by-product of manufacturing or industrial processes. Examples of these processes are tanneries, waste water treatment facilities, manure and sewage facilities, rayon manufacturing plants, sulfur producers, coke oven plants, kraft paper mills, iron smelters, food processing plants, tar and asphalt manufacturing plants, and natural gas and petrochemicals plants (Fuller and Suruda 2000).

Degradation of hydrogen sulfide in the atmosphere can occur through oxidation by oxygen (O_2) and ozone (O_3) to give sulfur dioxide (SO_2), and ultimately, sulfate compounds. Sulfur dioxide and sulfates

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



Derived from HazDat 2006

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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 life-times 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} cm³/molecule second (Cox 1975). Life-times 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 the reaction with ozone is not expected to be a significant environmental fate (Cox 1975).

Hydrogen sulfide oxidation by O₂ 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 (S²⁻), 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 (HSDB 2006).

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 also produced in the human large intestine and by the natural bacteria found in the human mouth (Richardson et al. 2000; Rosenberg et al. 1991). Populations living in areas of geothermal activity, or 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 are more likely to be exposed to higher levels of hydrogen sulfide. 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

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(Chénard et al. 2003; Devai and DeLaune 1999; Lehman 1996; Rimatori et al. 1996; Svendsen 2001); workers in these industries may be occupationally exposed to hydrogen sulfide.

6.2 RELEASES TO THE ENVIRONMENT

Hydrogen sulfide is not listed in the Toxics Release Inventory (TRI) as of September, 2005.

Hydrogen sulfide has been identified in a variety of environmental media (air, surface water, groundwater, soil, and sediment) collected at 35 of the 1,689 NPL hazardous waste sites (HazDat 2006).

6.2.1 Air

There is no information on releases of hydrogen sulfide to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005).

Hydrogen sulfide was identified in air collected at 23 of the 35 current or former NPL hazardous waste sites where it was detected in some environmental media (HazDat 2006).

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 hydrogeologically 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 Namibia and have been observed to affect areas of ocean surface of >20,000 km² (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/m²/hour from a spike grass site in the Everglades National Park in January 1986 and a sawgrass site

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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, textile plants, waste water treatment facilities, and tanneries (ACGIH 1991; 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 (ACGIH 1991; Bingham et al. 2001; HSDB 2006; Sittig 2002; Weil and Sandler 1997). Hydrogen sulfide may also be encountered in various industrial processes, such as the manufacture of dyes and pigments, felt, artificial silk, farming, 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 (HazDat 2006). Sulfides, including hydrogen sulfide, constitute up to 1% by volume of typical landfill gases (Agency for Toxic Substances and Disease Registry 2001). The Fresh Kills Landfill on Staten Island, New York has been estimated to release approximately 16 tons of hydrogen sulfide to the air annually (Agency for Toxic Substances and Disease Registry 2000). Facilities that treat manure may also release to 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 $5.7 \mu\text{g}/\text{m}^2/\text{second}$ (Lim et al. 2003).

6.2.2 Water

There is no information on releases of hydrogen sulfide to the water from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005).

Hydrogen sulfide has been identified in groundwater and surface water at 3 and 1 site, respectively, of the 35 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2006).

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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 (ACGIH 1991; 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 (ACGIH 1991; Bingham et al. 2001; HSDB 2006; Sittig 2002; Weil and Sandler 1997). Hydrogen sulfide may also be encountered in various industrial processes, such as the manufacture of dyes and pigments, felt, artificial silk, 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).

6.2.3 Soil

There is no information on releases of hydrogen sulfide to the soil from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005).

Hydrogen sulfide has been identified in soil at 13 sites and in sediment at 4 sites among the 35 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2006).

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).

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6.3 ENVIRONMENTAL FATE**6.3.1 Transport and Partitioning**

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 therefore, may partition as well 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 pHs ≤ 6 . At higher pHs, such as seawater, which has a pH of 8 or greater, 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.

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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, and its half-time in these environments usually ranges from 1 hour to several hours (Jørgensen 1982). Food chain bioconcentration and biomagnification are unlikely (HSDB 2006).

6.3.2 Transformation and Degradation

6.3.2.1 Air

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 life-times 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 $4.8 \times 10^{-12} \text{ cm}^3/\text{molecule second}$ (Cox 1975). Life-times 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 the reaction with ozone is not expected to be a significant environmental fate (Cox 1975).

6.3.2.2 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. 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%).

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Hydrogen sulfide oxidation by O₂ 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 1x10⁻⁷ 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 pHs of 7–9 (Boon 1992).

6.3.2.3 Sediment and Soil

Hydrogen sulfide is one of the 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 (SO₄²⁻). 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).

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to hydrogen sulfide depends in part on the reliability of supporting analytical data from environmental samples and biological specimens.

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Concentrations of hydrogen 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 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 in a variety of environmental media are detailed in Chapter 7.

6.4.1 Air

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/m³ and 1 ppb=1.40 µg/m³.

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, after 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 (Agency for Toxic Substances and Disease Registry 1997).

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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 the inside of the building. 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 at the central treatment plant final effluent box up to 340 ppm sulfur at the 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

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measured at detectable levels in only about half of the samples, with measured levels ranging from 2 ppb (the detection limit) to 33 ppb (Agency for Toxic Substances and Disease Registry 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, and 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 is 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).

Hydrogen sulfide levels in air on some NPL sites ranged from 0.00101 to 808 ppm at the Hartford Landfill in 1994 and at the Seattle Municipal Landfill in Washington in 1985, respectively (HazDat 2006). Data on ambient air concentrations at all NPL sites were not available, however. Concentrations of hydrogen sulfide in soil gas from samples taken at some NPL sites ranged from 0.29 to 47,000 ppm, reported at Holly Hill Resource Facility in Connecticut in 1999 and at the Industri-plex site in Massachusetts in 1990, respectively (HazDat 2006). Data on soil gas concentrations at all NPL sites were

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not available. It should be noted that concentrations in soil gas are likely to be higher than would be found in the breathing zone of an individual.

6.4.2 Water

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 pHs ≥ 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 Namibia. 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).

6.4.3 Sediment and Soil

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).

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6.4.4 Other Environmental Media

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, 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 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 6 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 brainstems 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 2 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;

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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 the OSHA, it was determined that high concentrations of hydrogen sulfide were apparently generated during the waste acid neutralization process (Smith and Cummins 2004).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

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), and 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 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).

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Residents of the Conimicut Point neighborhood in Warwick, Rhode Island were exposed to hydrogen sulfide from rotting seaweed and shellfish, after 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 wind into nearby neighborhoods (Agency for Toxic Substances and Disease Registry 2000).

Workers may be occupationally exposed to hydrogen sulfide from fermenting manure (Chénard et al. 2003; Morse et al. 1981), and stagnant wells (McDonald and McIntosh 1951), as well as in areas of waste-water treatment facilities (NIOSH 1980b, 1984, 1985a, 1985d, 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; HSDB 2006; Sittig 2002). Hydrogen sulfide may also be encountered in various industrial processes, such as 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).

Toxic exposure data for 1995, compiled from 67 poison control centers, indicated that there were 1,407 hydrogen sulfide exposures during that year, 3 of which were intentional exposures (Litovitz et al. 1996). None of these individuals died, and the vast majority of these exposures resulted in outcomes that were either minor or nonexistent. Approximately 34% of the exposed individuals were treated in a health care facility (Litovitz et al. 1996).

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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. 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 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 is found naturally in crude petroleum, natural gas, volcanic gases, hot springs, and often as the result of bacterial breakdown of organic matter. Children are more likely to be exposed to hydrogen sulfide near animal waste sites such as the sediments of fish aquaculture, livestock barns, or manure areas. Inhalation is the most likely route of exposure, and there are no known exposure pathways that are unique to children, although hydrogen sulfide is heavier than air so that children might be exposed 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. 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

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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).

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

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.

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 is available. Where adequate information is not available, ATSDR, in conjunction with NTP, is required to assure the initiation of a program of

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research designed to determine the health effects (and techniques for developing methods to determine such health effects) of hydrogen 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. Information is available on the physical and chemical properties of hydrogen sulfide (Al-Haddad et al. 1989; Amoores and Hautala 1983; Daubert and Danner 1989; HSDB 2006; NIOSH 2006; 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.

Production, Import/Export, Use, Release, and Disposal. Adequate information on the production and use of hydrogen sulfide was found; no information on the import/export of hydrogen sulfide was located. Since hydrogen sulfide is not required to be reported under the TRI, the production and emissions from U.S. industrial facilities is not reported to the EPA. Information of production, emissions, and disposal would be useful in identifying important processes leading to human exposure.

Environmental Fate. 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.

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 this route of exposure for populations of concern.

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Food Chain Bioaccumulation. Sufficient information is available to demonstrate that hydrogen sulfide is not likely to bioaccumulate or biomagnify in the food chain.

Exposure Levels in Environmental Media. Reliable monitoring data for the levels of hydrogen sulfide in 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 burden of hydrogen sulfide to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

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.

Exposure Levels in Humans. 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.

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-

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containing compounds and particulates. Additional exposure information is needed from communities where only hydrogen sulfide exceeds background levels.

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 were located. This substance is not currently one of the compounds for which a sub-registry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for sub-registries 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 this substance.

6.8.2 Ongoing Studies

No ongoing studies pertaining to the environmental fate of hydrogen sulfide were identified in a search of the Federal Research in Progress database (FEDRIP 2005).