

## 5. POTENTIAL FOR HUMAN EXPOSURE

### 5.1 OVERVIEW

Sulfur dioxide has been identified in at least 16 of the 1,467 current or former EPA National Priorities List (NPL) hazardous wastes sites (HazDat 1998). However, the number of sites evaluated for sulfur dioxide is not known. The frequency of these sites within the United States can be seen in Figure 5-1.

Atmospheric sulfur dioxide is formed as a by-product of the combustion of fuel from power generation and industrial activities, and by the oxidation of reduced gases in the atmosphere. Volcanic activity also contributes to the levels of atmospheric sulfur dioxide. The atmospheric lifetime of sulfur dioxide is about 10 days (IARC 1992).

Sulfur dioxide is oxidized rapidly by both homogeneous and heterogeneous reactions and is removed from the atmosphere by precipitation and by dry deposition on surfaces, mainly as sulfuric acid.

Inhalation of sulfur dioxide, by the general population residing near industrial sources and by workers exposed to sulfur dioxide, is generally the main route of human exposure to the chemical.

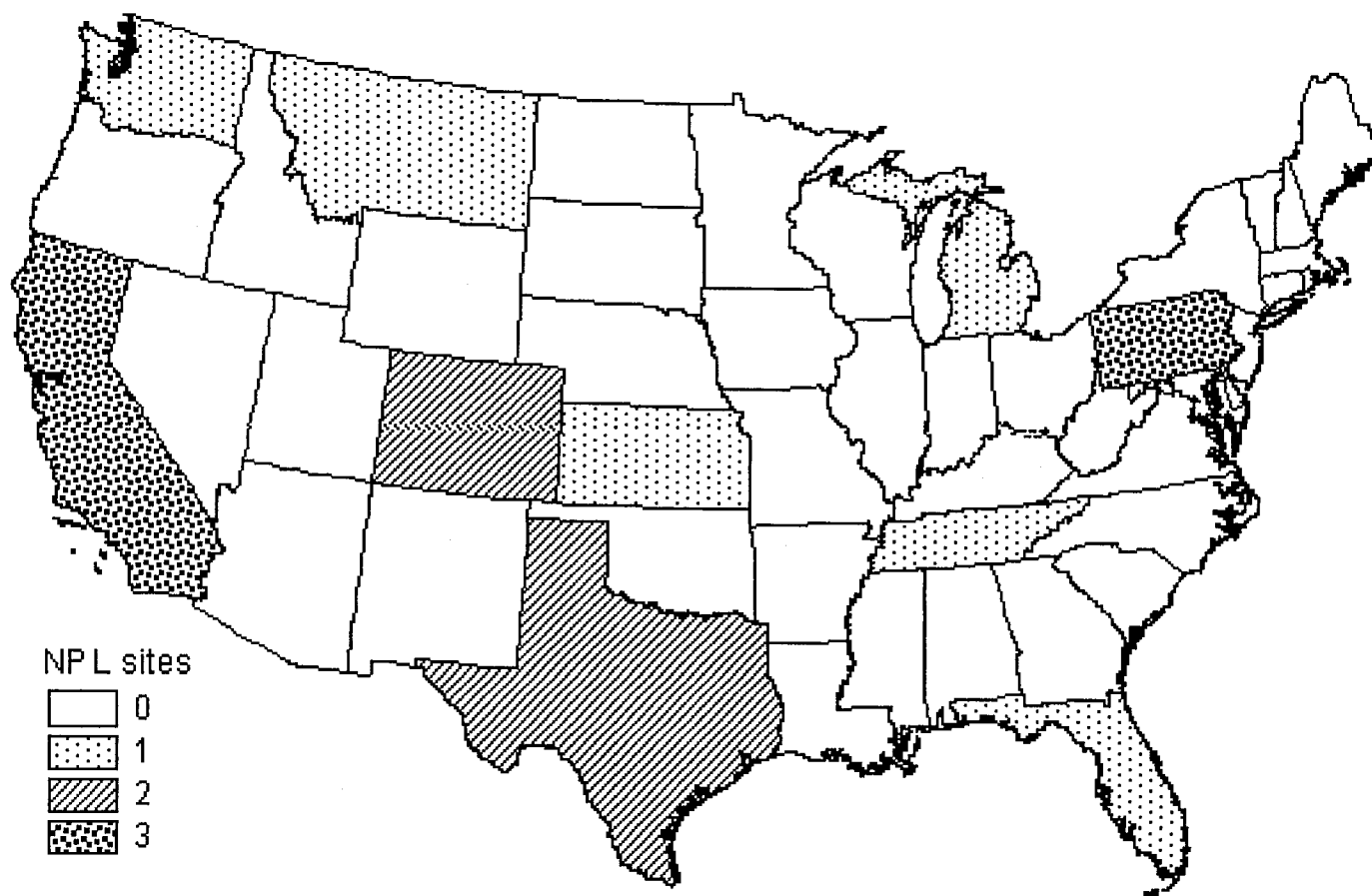
It should be noted that the amount of sulfur dioxide detected by chemical analysis is not necessarily the amount that is bioavailable.

### 5.2 RELEASES TO THE ENVIRONMENT

Releases of sulfur dioxide to the environment from large processing facilities are not required to be reported to the Toxics Release Inventory (TRI).

Releases of sulfur dioxide are not required to be reported under SARA Section 313. Consequently, there are no data for this compound in the current TRI. Sulfur dioxide has been identified in a variety of environmental media (air, surface water, groundwater, soil, and sediment) collected at 16 of the 1,467 NPL hazardous waste sites (HazDat 1998).

Figure 5-1. Frequency of NPL Sites With Sulfur Dioxide Contamination



\* Derived from HazDat 1998

### 5.2.1 Air

Releases of sulfur dioxide to air from large processing facilities are not required to be reported to the Toxics Release Inventory (TRI).

Sulfur dioxide has been identified in air samples collected at 8 of the 16 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

Atmospheric sulfur dioxide, a major oxide of sulfur, can be formed from both anthropogenic and natural sources. On a global scale, the total annual atmospheric flux of sulfur has been estimated to be 140-350 million tons (of which less than 30% is anthropogenic sulfur) in the form of sulfur dioxide, sulfuric acids, and sulfate (HSDB 1998). The primary anthropogenic source of sulfur dioxide gas is fuel combustion from power generation and industrial processes. Fossil fuel accounts for 75-85% of man-made sulfur dioxide emissions on a global scale; industrial processes such as refining and smelting account for the remainder (HSDB 1998). Almost all of the man-made sulfur dioxide emissions (93.5%) are released in the Northern Hemisphere (HSDB 1998). With regard to the United States, EPA National Air Pollutant Emission Trends estimate that in 1994 a total of 2 1.1 million tons of sulfur dioxide was emitted into the atmosphere in the United States from point and area sources (EPA 1994a). The Air Toxicities Program is striving to reduce toxic air pollutants emissions in the United States by 1.5 million tons annually over the next 10 years (EPA 1995). Of the total sulfur dioxide emissions, about 18.5 million tons or 87.6% was attributed to fuel combustion, of which electricity utilities and industrial combustion constituted about 70% and 14%, respectively (EPA 1994a). The Utility Air Toxicities Study examines hazardous air pollutant emissions from coal, oil, and gas (fossil fuel) electric utilities and associated public health hazards. The predictions for the next two decades are a 30% increase in hazardous air pollutant emissions from coal utilities and a 50% decrease in emissions from oil utilities (EPA 1995). Sulfur dioxide emission from fuel combustion have come primarily from coal burning, with coal combustion producing 96% of the electric utility emissions. A similar trend was observed in England (Lee and Longhurst 1993), but not in Denmark where road traffic was considered the most prevalent source of air pollution for sulfur dioxide (Jensen and Fenger 1994).

According to EPA's National Air Pollutant Emission Trends (EPA 1994a), other sources of sulfur dioxide include emissions from chemical and allied product manufacturing, metal processing, petroleum and related industries, other industrial processes, and on-road vehicles. These sources are, however, of less importance

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as they collectively contributed less than 13% of the total emissions (EPA 1994a). Since sulfur dioxide is the major substance used for manufacturing sulfuric acid, it is not surprising that a significant source of industrial emissions is acid manufacturing and processing facilities.

Data are available at the state-level for sulfur dioxide emissions and rank by major category (EPA 1994a). Ohio and Indiana ranked first and second in the total sulfur dioxide emissions. Fuel combustion for electrical utilities accounted for the greatest portion of total emissions in all states. On the national level, sulfur dioxide emissions have shown a steady decrease in the United States since the 1970s (EPA 1994a; Lefohn and Shadwick 1991).

A study was conducted among 24 United States communities to study air pollution patterns (Spengler et al. 1996). A strong correlation between particle mass and sulfate concentrations and sulfate and hydrogen ion concentrations was found in Ohio, Pennsylvania, Virginia, West Virginia, Tennessee, and Kentucky. Concentrations in these areas ranged between 85 and 126 nmol/m<sup>3</sup> in the summer, the highest being in Ohio, Pennsylvania, and Kentucky. Due to the meteorological conditions, acidic pollution is highest during summer months in these areas. Sulfur dioxide is converted to acid sulfates without the presence of ammonia during this time (Spengler et al. 1996).

The Acid Rain Program projects a 40% reduction in SO<sub>2</sub> annual emissions in the United States between 1980 and 2010. The U.S. Geological Survey reports a 10 to 25% reduction in acidic rainfall because of a decline in emissions due to the Acid Rain Program. This reduction in emissions will also contribute to less sulfate haze (EPA 1995).

Volcanoes are a sporadic, but significant, natural source of sulfur dioxide. It has been estimated that 1.5x10<sup>6</sup> tons of sulfur dioxide per year were evolved from worldwide volcanic production between the years 1500 and 1914 (Kellogg 1972). This estimate is about two orders of magnitude lower than the total annual sulfur dioxide liberated to the atmosphere (Kellogg 1972).

### 5.2.2 Water

Releases of sulfur dioxide to water from large processing facilities are not required to be reported to the Toxics Release Inventory (TRI).

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Sulfur dioxide is very soluble in water, and the oceans are generally considered to be a sink for sulfur dioxide (Kellogg 1972). Surface water bodies can receive sulfur dioxide from the atmosphere by dry and wet deposition, from surface runoff, and from subsurface drainage (HSDB 1996; IARC 1992; Kellogg 1972; WHO 1979). It has been estimated that 70% of sulfate in rainwater comes from the washout of sulfur dioxide (Kellogg 1972). Hydrogen sulfide present in the oceans is probably oxidized to sulfur dioxide within hours (HSDB 1998). Rivers can transport sulfur compounds to the oceans (HSDB 1996).

It is possible that oceans may be a source of sulfur dioxide, especially during conditions when the equilibrium vapor pressure of sulfur dioxide in surface water exceeds the partial pressure of sulfur dioxide in the air immediately above it (Kellogg 1972). Sea salt can contribute to atmospheric levels of sulfate (Kellogg 1972).

There is no information on releases of sulfur dioxide to water from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997).

### 5.2.3 Soil

Releases of sulfur dioxide to soil from large processing facilities are not required to be reported to the Toxics Release Inventory (TRI).

Sulfur dioxide has been identified in soil and sediment samples collected at 5 of the 16 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

Atmospheric sulfur dioxide can be removed by diffusion to the soil (Kellogg 1972). Sulfur uptake is dependent upon soil pH and moisture content (Kellogg 1972). One estimate of the uptake of sulfur dioxide by soil and vegetation is  $52 \times 10^6$  tons per year (Kellogg 1972). A rate of diffusion of  $0.9 \times 10^{-12}$  g/s  $\text{cm}^2/\text{second}$  has been calculated for the Northern Hemisphere (Kellogg 1972).

There is no information on releases of sulfur dioxide to soil from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997).

### 5.3 ENVIRONMENTAL FATE

#### 5.3.1 Transport and Partitioning

Anthropogenic and natural releases of sulfur dioxide to the environment are considered to be primarily to the atmosphere (HSDB 1998; Kellogg 1972; WHO 1979). Because of its high vapor pressure (3,000 mm Hg at 20°C), sulfur dioxide is typically present in a gaseous phase. Some of the sulfur dioxide emitted into the air moves unchanged to various surfaces including soil, water, grass, and vegetation in general (WHO 1979). In the atmosphere, sulfur dioxide can be transformed into sulfuric acid or sulfates by a variety of processes (WHO 1979).

A field deposition study in Canada was conducted to measure the effects of atmospheric stability, rainfall intensity, and wind speed and direction on SO<sub>2</sub> deposition. The object was to compare the field data with the modeled results from a computation of the SO<sub>2</sub> contamination and accumulation by forests downwind from an SO<sub>2</sub> source. The highest levels of SO<sub>2</sub> deposition were found along the north-south direction and low levels were found along the northwest direction. This is due to the fact that the wind direction from north-south is consistent with neutral weather, and wind direction from northwest is consistent with rainy weather and airborne SO<sub>2</sub> scavenging. The final results show that the field data is comparable to the modeled data; the modeled results accurately describe the deposition patterns in relation to the weather patterns and is therefore considered a reliable source (Bouque et al. 1996).

Sulfur dioxide is very soluble in water, and oceans are generally considered to be a sink for sulfur dioxide (Kellogg 1972). It is also possible that oceans can be a source of sulfur dioxide if the equilibrium pressure of sulfur dioxide in surface water exceeds the partial pressure of sulfur dioxide in the air immediately above it. Any potential releases of sulfur dioxide from water would be expected to partition to the atmosphere as discussed in Section 5.3.2.1 (Kellogg 1972; WHO 1979).

Soil can absorb sulfur dioxide, with uptake being dependent on the pH and moisture content of the soil (HSDB 1998). No data were found pertaining to soil adsorption and mobility of sulfur dioxide in soil. Hill (1971) studied absorption of several gaseous air pollutants by plants and found that the removal rates were in the following order: hydrogen fluoride (HF) > sulfur dioxide (SO<sub>2</sub>) > chlorine (Cl<sub>2</sub>) > nitrogen dioxide (NO<sub>2</sub>) > ozone (O<sub>3</sub>) > peroxyacetyl nitrate (PAN) > nitric oxide (NO) > carbon monoxide (CO).

### 5.3.2 Transformation and Degradation

#### 5.3.2.1 Air

Sulfur dioxide may be oxidized to sulfur trioxide (SO<sub>3</sub>) and sulfate in air photochemically or catalytically (Bufalini 1971; Radojevic 1992). The oxidations generally involve homogeneous-phase reactions (oxidation in the gas phase) and heterogeneous gas-solid reactions (oxidation on the surface of particles). Gas-phase reactions include direct photochemical oxidation of sulfur dioxide and oxidation by reacting with other gases and substances, including O, O<sub>2</sub>, O<sub>3</sub>, NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, OH, hydrocarbons, or some heavy metal ions. In the direct oxidation pathway, sulfur dioxide gas molecules (at different electronically excited states due to solar irradiation) react with each other, forming SO<sub>3</sub>, which may be further oxidized by other gases or water drops to form sulfate. Reaction pathways with other gases all result in similar end products: SO<sub>3</sub>, or sulfate. Rate constants for sulfur dioxide oxidation by these gases vary from  $2 \times 10^{-24}$  to  $4 \times 10^{-3}$  cm<sup>3</sup> molecule<sup>-1</sup> second<sup>-1</sup>, with the reaction with N<sub>2</sub>O<sub>5</sub> being the fastest (Radojevic 1992). Heterogeneous gas-solid reactions include oxidation of sulfur dioxide on the surfaces of activated carbons, metal oxides, and other particles.

Sulfur dioxide may be photochemically or catalytically oxidized to SO<sub>3</sub> and sulfate in air (Bufalini 1971; Radojevic 1992). The oxidations generally involve homogeneous-phase reactions (oxidation in gas or liquid phase) and heterogeneous gas-solid reactions (oxidation on the surface of particles). The atmospheric residence time of sulfur dioxide is about 10 days. Photochemical oxidation involves the reaction of sulfur dioxide with reactive molecules and free radical species, and with products of O<sub>3</sub> and alkene gases. Photochemical oxidation is thought to be initiated by absorption of solar irradiation energy. However, neither the detailed mechanism of this process nor the significance of this conversion process is clear. Photochemical oxidation was previously thought to be insignificant because the maximum conversion rate of sulfur dioxide was considered to be <0.04% h<sup>-1</sup> (Calvert et al. 1978; Radojevic 1992). However, much higher conversion rates (0.65% h<sup>-1</sup>) were reported by other researchers (Cox and Penkett 1970), and it was suggested that trace impurities in the ambient air may have contributed to this.

Sulfur dioxide can be oxidized by OH radicals in the gas phase relatively quickly, making it a major mechanism for sulfur dioxide conversion. This is a three-body addition reaction, and the conversion rates have been characterized to be >1% hour<sup>-1</sup> (Radojevic 1992).

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In the atmosphere, aqueous-phase oxidation of sulfur dioxide can occur in cloud, fog, rain, deliquescent aerosol particles, and in surface liquid films on these particles (Benner et al. 1992; McKay 1971). Once dissolved in these droplets, sulfur dioxide may be oxidized to sulfate via a variety of mechanisms, thus forming "acid rain." Such a removal mechanism is commonly termed "wet deposition." The conditions under which this oxidation can be enhanced have been studied (Barrie and Georgii 1976). The investigators found that the absorption of sulfur dioxide was facilitated by manganese and iron ions, high solution pH, and high temperature. A decrease in temperature from 25 °C to 8°C resulted in a 5-10-fold decrease in sulfur dioxide absorption rates. It was estimated that typical sulfur dioxide removal rates through this mechanism were between 0.08% and 2.0% hour<sup>-1</sup> depending on the manganese and iron concentrations and temperature. The catalytic oxidation of sulfur dioxide in the presence of iron and manganese was, however, not supported by Fung et al. (1991), who investigated the relative importance of three major aqueous reactions thought to be responsible for the in-cloud conversion of sulfur dioxide: oxidation of sulfur dioxide by H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> or O<sub>2</sub><sup>-</sup>; in the presence of iron and manganese. They found that sulfate precipitation concentration is generally more sensitive to H<sub>2</sub>O<sub>2</sub> than to O<sub>3</sub>, and that the contribution of iron and manganese in the oxidation of sulfur dioxide by O<sub>2</sub><sup>-</sup> is insignificant. Some research has shown that catalyzed liquid-phase oxidation in the presence of iron and manganese is important in urban plumes and fogs where sulfur dioxide concentrations are sufficiently high; this oxidation may not be significant in cleaner, rural areas (HSDB 1998). The average overall conversion rate of sulfur dioxide (through all processes) to sulfate in Beijing was estimated to be 4.7% hour<sup>-1</sup> during the day and 3.4% hour<sup>-1</sup> during the night (Chen et al. 1990).

In a study of acid rain chemistry in the Allegheny Mountains, it was found that on average about half of the rain sulfate resulted from the scavenging of sulfur dioxide and the other half resulted from aerosol sulfate. Most of the rain acidity (~80%) arose from gases dissolved in cloudwater and rainwater (Pierson et al. 1987).

Sulfur dioxide can also be oxidized by some particles; this heterogeneous oxidation is affected by oxidants other than O<sub>3</sub>, temperature, and humidity. Particles that can react with and oxidize sulfur dioxide include carbonaceous metal oxides, atmospheric particles, and other particles (Radojevic 1992).

Sulfur dioxide can also be removed from air by uptake of plant leaves. It is reported that direct surface uptake of sulfur dioxide is the most significant dry removal process for atmospheric sulfur (HSDB 1998). A study of the absorption of several gaseous air pollutants by plants found that the removal rates were in the following order: hydrogen fluoride (HF) > sulfur dioxide (SO<sub>2</sub>) > chlorine (Cl<sub>2</sub>) > nitrogen dioxide (NO<sub>2</sub>) > ozone (O<sub>3</sub>) > peroxyacetyl nitrate (PAN) > nitric oxide (NO) > carbon monoxide (CO) (Hill 1971).



### 5.3.2.2 Water

It has been known for a long time that sulfur dioxide in air can be oxidized to sulfate by cloud or rain droplets, thus forming “acid rain.” Barrie and Georgii (1976) studied the conditions under which this oxidation can be enhanced. They found that the absorption of sulfur dioxide was facilitated by manganese and iron ions, high solution pH, and high temperature. A decrease in temperature from 25°C to 8°C resulted in a 5-10-fold decrease in sulfur dioxide absorption rates. It was estimated that typical sulfur dioxide removal rates through this mechanism were between 0.08% and 2.0% hour<sup>-1</sup>, depending on the manganese and iron concentrations and temperature.

In addition to the above factors, oxidation of sulfur dioxide to sulfate is also affected by many dissolved gases. The oxidation normally involved reactions with dissolved H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, OH<sup>-</sup>, HSO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, H<sub>3</sub>COOH, O<sub>3</sub>, HO<sub>2</sub>, NO<sub>2</sub>, NO<sub>3</sub>, NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, NH<sub>2</sub><sup>-</sup> and peroxyacetyl nitrate (PAN), with some reactions catalyzed by F<sup>3+</sup> or Mn<sup>2+</sup> (Benner et al. 1992; McKay 1971). All of these reactions are dependent on solution pH because pH affects the solubility of sulfur dioxide. Benner et al. (1992) reported that oxidation of sulfur dioxide to sulfate was greatly enhanced when cloud droplets were exposed to sulfur dioxide and NH<sub>3</sub>. Speculating that the enhanced surface oxidation may be true for NH<sub>3</sub>, Benner et al. (1992) further studied the phenomenon and found that sulfur dioxide can be oxidized to sulfate only when NH<sub>3</sub> is present. This led to the conclusion that sulfur dioxide can be oxidized more rapidly in the presence of both sulfur dioxide and NH<sub>3</sub>, compared to sulfur dioxide alone. Fung et al. (1991) determined the relative importance of three major aqueous reactions through which sulfur dioxide is oxidized to sulfate and found that oxidation by H<sub>2</sub>O<sub>2</sub> was stronger than O<sub>3</sub>, oxidation in light precipitation areas and was comparable in heavy precipitation areas. The contribution of catalytic oxidation of O<sub>2</sub><sup>-</sup>; in the presence of manganese and iron was insignificant in any occasion.

The current practices in diluted acids disposal include discharging to waste-water treatment plants or neutralization by calcium hydroxide, which produces gypsum that can be reused. Stucki et al. (1993) developed an alternative disposal technique for sulfuric acid and a new combination of recycling processes. This technique involves reducing sulfuric acid to volatile weak acids by sulfate-reducing bacteria.

Dissolved sulfur dioxide in the surface layer of the ocean may be slowly oxidized to the sulfate anion (SO<sub>4</sub><sup>2-</sup>) by the combined presence of dissolved O<sub>2</sub> and trace amounts of transition metal salts as catalysts (Kellogg 1972). At ocean depths, dispersed sulfate may be reduced to sulfur dioxide, sulfur, and hydrogen sulfide by the action of bacteria (Kellogg 1972).

Sulfur dioxide absorbed by freshwater lakes is less rapidly oxidized than seawater because of the much lower salt content of freshwater (Kellogg 1972).

### 5.3.2.3 Sediment and Soil

Once on the ground, sulfur dioxide may be absorbed by soil, water, and snow-covers (HSDB 1998; WHO 1979). Although snow-covered surfaces are ineffective in absorbing gaseous and particulate sulfur compounds, the melted snowpack during spring can result in rapid, short-term inputs of high sulfate into fresh water.

Sulfur dioxide can be reduced to H<sub>2</sub>S in heat- and alkali-treated sewage sludge by the sulfate-reducing bacteria, *Desulfovibrio desulfuricans* or *Desulfotomaculum orientis* (Deshmane et al. 1993).

Acid rain is the leading cause in an increase in heavy metal mobility in soil. When soil is basic pH, heavy metals will form insoluble oxides or hydroxides of sulfate, and when soil is acidic, soluble sulfates will form (Grzesiak et al. 1997).

Hill (1971) and Garland et al. (1973) reported that vegetation could be an important sink for sulfur dioxide and several other air pollutants. Plants can absorb sulfur dioxide from air. Siebke et al. (1990) developed a model for simulating uptake and metabolism of sulfur dioxide by different leaf cell compartments.

## 5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to sulfur dioxide depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing data on sulfur dioxide 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 sulfur dioxide in a variety of environmental media are detailed in Chapter 6 (Analytical Methods).

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**5.4.1 Air**

Sulfur dioxide has been detected in urban, rural, and remote areas of the world (Kirk-Othmer 1978). Worldwide emissions of about 70.7 million tons of sulfur in the form of SO<sub>2</sub> were estimated for 1994 (O'Meara 1997). However, sulfur dioxide concentrations in the atmosphere display a very large range, depending on the intensity of industrial and urban development. It has been estimated that sulfur dioxide concentrations can range from 1 to 5 µg/m<sup>3</sup> (0.0004-0.0019 ppm) in very remote clean areas to at least 6,000 µg/m<sup>3</sup> (2.29 ppm) in industrial areas (HSDB 1998). Trends show that in the United States between 1986 and 1995 the national composite SO<sub>2</sub> average decreased 37% and SO<sub>2</sub> emissions decreased 18%. Between 1994 and 1995 SO<sub>2</sub> emissions decreased 13% and mean national concentrations decreased 17% (EPA 1995). Spengler et al. (1990) reported that about 80% of U.S. sulfur dioxide emissions come from within the 31 states bordering on, or located east of the Mississippi River.

Higher concentrations of sulfur dioxide have been detected during forest fires and volcano eruptions. In response to a request from the Hawaii State Health Department, NIOSH made an assessment of exposure to lava and seawater emissions resulting from lava flowing into the sea, vaporizing the seawater, and releasing some toxic gases. Sulfur dioxide was detected at about 1.5 ppm in visible plumes (NIOSH 1992a). At the request of the National Park Services, NIOSH (1992b, 1992c) measured concentrations of several toxic gases at the personal breathing zone on July 18, 1991, as a result of a forest fire. Sulfur dioxide concentrations ranged from 0.6 to 3.0 ppm, with three samples above the evaluation criteria. On another occasion, firefighters' exposures to chemical contaminants during fire suppression operations were found to be as high as 9 ppm for sulfur dioxide (NIOSH 1991). These concentrations were close to or above the current NIOSH sulfur dioxide time-weighted-average (TWA) exposure limit of 2 ppm (NIOSH 1997) and above the shortterm exposure limit (STEL) of 5 ppm.

**5.4.2 Water**

No data were located regarding levels of sulfur dioxide monitored or estimated in water.

**5.4.3 Sediment and Soil**

No data were located regarding levels of sulfur dioxide monitored or estimated in sediment or soil.

#### 5.4.4 Other Environmental Media

Sulfur dioxide can be taken up from the atmosphere by sulfate-treated plants. However, no estimates of the levels of sulfur dioxide are available (HSDB 1998). Sulfur dioxide has been detected in various foods and beverages (IARC 1992). Table 5-1 summarizes the levels of sulfur dioxide in several foods and beverages.

### 5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Since sulfur dioxide is primarily present in gaseous form, the general public is exposed to it mostly by inhaling contaminated air. Exposures would be expected to be highest near industrial activities that involve fuel combustion. The well-known air pollution disaster that occurred in London in December of 1952 exemplifies the extent to which the general population has been exposed to adverse levels of sulfur dioxide in past years (IARC 1992; WHO 1979). Excess mortality was observed during this episode but several other contaminants were also present in air during the pollution episode. Other well-known examples of serious air pollution episodes include those that occurred in Meuse Valley, Belgium, and Donora, Pennsylvania (IARC 1992; WHO 1979). Table 5-2 summarizes ambient air levels of sulfur dioxide in various parts of the world.

Occupational exposures to sulfur dioxide are associated with workers in steel processing, refinery, and chemical plants. These workers are also frequently exposed to acid mists with increased risk of laryngeal cancer (Ahlborg et al. 1981; Forastiere et al. 1987; Soskolne et al. 1984; Steenland et al. 1988). It has been estimated that approximately 600,000 American workers may be occupationally exposed to sulfur dioxide (HSDB 1998). Some of the highest exposures occur when it is a by-product, as in the metal smelting industry, and in the processing or combustion of high-sulfur coal or oil (HSDB 1998).

Levels of occupational exposure vary from industry to industry. Sulfite pulp worker exposure fluctuates but reached levels greater than 10 ppm (26 mg/m<sup>3</sup>) in the 1950s (studies in Finland, Norway, and the United States) (IARC 1992). Because of modernization of facilities and processes, these levels have been falling. Roasting of ores and the combustion of sulfur-containing fuels in the metal industries have resulted in workplace exposure concentration means of 1-10 ppm (2.6-26 mg/m<sup>3</sup>) in copper smelters (studies in the following countries with corresponding years of measurement: Finland, 1951-1957; Sweden, date not specified; United States, 1940-1974, 1976, 1982) and 1 ppm (2.6 mg/m<sup>3</sup>) or less in other operations. Occupational exposure levels with a mean >1 ppm (2.6 mg/m<sup>3</sup>) have been measured during sulfuric acid and superphosphate fertilizer manufacture as well as during firefighting (IARC 1992).

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**TABLE 5-1. Levels of Sulfur Dioxide in Various Foods and Beverages<sup>a</sup>**

Food/beverage	Concentration of Sulfur Dioxide (ppm)
Onions, fresh	17
Onions, dried	60
Onions, canned, boiled	4
Onions, dried soup mix	10–30
Garlic, dried	121
Leak, dried soup mix	7
Soya bean protein, nonsulfited	20
Soya bean protein, sulfited	80–120
Cherries	24
Wine, white	14
Wine, burgundy	150

<sup>a</sup>IARC 1992

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**TABLE 5-2. Ambient Air Concentrations of Sulfur Dioxide in Different Parts of the World<sup>a</sup>**

Location	Year	Sulfur dioxide concentration ( $\mu\text{g}/\text{m}^3$ )
Rural New York	1984–86	3.38–7.44 (0.0013–0.0028 ppm)
Pennsylvania	1983	26–31 (0.01–0.012 ppm)
Rural Pennsylvania	1984	3–131 (0.0011–0.05 ppm)
Bermuda	1982–83	0–1.67 (0–0.0006 ppm)
Coastal Delaware	1985	13.4 (0.005 ppm)
Bermuda (mid-ocean)	1985	0.7 (0.00027 ppm)
Northwest Territories, Canada	November–December 1981	0.33–0.69 (0.00013–0.00026 ppm)
Northwest Territories, Canada	February 1982	2.3–4.3 (0.00088–0.0016 ppm)
Ontario, Canada	1982	8.4–16.2 (0.0032–0.0062 ppm)
Ontario, Canada	1984	0.1–62.8 (0–0.024 ppm)
Near H <sub>2</sub> SO <sub>4</sub> producer, United Kingdom	1981	0.5–120 (0.0002–0.046 ppm)

<sup>a</sup>IARC 1992

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Other probable exposure routes are dermal and/or eye contact (HSDB 1998). Since sulfur dioxide is an irritating, corrosive gas, direct dermal or ocular contact can cause immediate damage. The general public can also be exposed to sulfur dioxide through ingestion of some foods that contain it such as onion, garlic, and wine (see Table 5-1).

According to the National Occupational Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983, an estimated 55,029 workers were potentially exposed to sulfur dioxide in the workplace (NOES 1990). The NOES database does not contain information on the frequency, concentration, or duration of exposure; the survey provides only estimates of the number of workers potentially exposed to chemicals in the workplace.

No information was found regarding the number of people potentially exposed in the vicinity of hazardous waste sites. However, since sulfur dioxide has been found near hazardous waste sites, people living near them may be exposed to higher than background levels.

### 5.6 EXPOSURE OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans and briefly considers potential pre-conception exposure to germ cells. Differences from adults in susceptibility to hazardous substances are discussed in 2.6 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, and 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; they put things in their mouths; they may ingest inappropriate things such as dirt or paint chips; they spend more time outdoors. Children also are closer to the ground, and they do not have the judgement of adults in avoiding hazards (NRC 1993).

Sulfur dioxide is a common air pollutant, and children of all ages are therefore potentially exposed. Inhalation is the primary route of exposure and there are no known exposure pathways that are unique to children. Children living near NPL waste sites or in areas of heavy industry, such as those related to fuel combustion, metal processing, and paper manufacturing, are typically exposed to the highest concentrations

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of sulfur dioxide. Levels of sulfur dioxide in air vary between 1-5  $\mu\text{g}/\text{m}^3$  (0.0003-0.002 ppm) in rural areas and 6,000  $\mu\text{g}/\text{m}^3$  (2.3 ppm) in industrial areas (HSDB 1998). Significant exposures are not anticipated through diet, household products, structural building materials, school activities, or the clothing, skin, or breath of occupationally exposed parents.

There are no known studies which report levels of sulfur dioxide or its metabolites in children, in maternal reproductive organs during pregnancy, or in breast milk. The weight adjusted intake of sulfur dioxide in children compared to adults is not known but may be greater. Children breath more air per kilogram of body weight than adults. Children exercise more frequently than adults (CDC 1996; Cureton 1987). Exercise increases breathing rate and results in both an increased dose of sulfur dioxide to the lower respiratory tract and enhanced pulmonary effects. Studies which measure weight-adjusted intake in children have not been identified.

Exposure to children can be reduced by limiting the time spent outdoors, especially during periods of high pollution levels. Studies in animals indicate that small quantities of sulfur dioxide metabolites reach the gonads following inhalation of sulfur dioxide. The chemical identity of the metabolites is not known (i.e., sulfite, *S*-sulfonate, sulfate), but animal studies indicate that genotoxic effects in germ cells are unlikely following inhalation of sulfur dioxide. There is no available information on whether sulfur dioxide metabolites are likely to cross the placenta or be transferred to breast milk.

### 5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to individuals who are occupationally exposed to sulfur dioxide (see Section 5.5), there are several groups within the general population that have potentially high exposures (higher than background levels) to sulfur dioxide. These populations include individuals living in proximity to sites where sulfur dioxide was produced or sites where sulfur dioxide was disposed of, and individuals living near one of the 16 NPL hazardous waste sites where sulfur dioxide has been detected in some environmental media (HazDat 1998).

Workers involved in industries in which sulfur dioxide is processed or produced are at a potential risk to high sulfur dioxide exposures. Some of the highest exposures occur during the processing or combustion of high-sulfur coal or oil. Members of the general population who live near urban areas with industrial activities related to the processing or combustion of high-sulfur fuels would be exposed to higher than background levels of sulfur dioxide.



## 5.8 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 sulfur dioxide is available. Where adequate information is not available, ATSDR, in conjunction with the 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 sulfur dioxide.

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.

### 5.8.1 Identification of Data Needs

**Physical and Chemical Properties.** Adequate information is available on the physical and chemical properties of sulfur dioxide (HSDB 1998).

**Production, Import/Export, Use, Release, and Disposal.** According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 USC. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1993, became available in May of 1995. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

However, sulfur dioxide is not required to be reported to the TRI. There are some estimates of the release of sulfur dioxide to the environment from anthropogenic sources on a global scale. There are also some estimates of national emissions of sulfur dioxide (EPA 1994a). Additional information on the identification of the sources that are likely to produce 5- and 10-minute peak exposures to high concentrations of sulfur dioxide, as well as on the frequency of the occurrence of such peak exposures, would be useful.

## 5. POTENTIAL FOR HUMAN EXPOSURE

The latest import information reported was for 1994 (NTDB 1996) and the latest export information was for 1996 (NTDB). More recent import/export information would be useful.

**Environmental Fate.** There are no accurate measurements of the releases of sulfur dioxide from natural sources such as volcanoes, the ocean, and biogenic sources (Kellogg 1972; WHO 1979). Crude estimates of the release of sulfur dioxide from natural sources have been based on the amount of sulfur required to balance the total sulfur budget (Kellogg 1972). Studies that can provide more accurate estimates of the releases of sulfur dioxide from natural sources would be useful. Also, additional information on the role of sulfur dioxide released from anthropogenic and natural sources in the formation of acid rain would be useful.

Releases of sulfur dioxide to the environment as a result of industrial activity are expected to be primarily to the atmosphere (WHO 1979). Atmospheric sulfur dioxide is formed as a by-product of the combustion of fuel from power generation and industrial activities, and by the oxidation of reduced gases in the atmosphere. Since water covers 70% of the earth's surface, biogenic gas emissions are the largest natural source of sulfur emissions to the atmosphere. Airborne sea spray and marine and coastal organisms are all responsible for introducing sulfur into the atmosphere. These emissions are estimated at 11.9 and 15.4 Tg S gases/year (Tg = teragrams =  $10^{12}$ g; S = sulfur) according to the Department of Energy (DOE 1996). Volcanic activity also contributes to the levels of atmospheric sulfur dioxide (Kellogg 1972). Gas emissions by vulcanism have shown estimates which vary due to methods of measurement and vulcanism variability. The annual volcanic sulfur emissions range was between 0.75 and 42 Tg S. However, the more well known median estimates were 9-24 Tg S/year with the average annual value being  $\geq 9$  Tg S (DOE 1996). Sulfur dioxide is oxidized rapidly by both homogeneous and heterogeneous reactions and is removed from the atmosphere by precipitation and by dry deposition on surfaces, mainly as sulfuric acid. A 1983 study by Ryaboshapko found that, based on seasonality, area1 distribution, mixing height and other factors, annual global wind blown soil sulfur emissions were 3.3-10 Tg S/year with an average of 6.7 Tg S/year. These emissions are more significant for some arid and semi-arid regions (DOE 1996). Additional information on the half-life of sulfur dioxide in soils and water would be useful.

**Bioavailability from Environmental Media.** Sulfur dioxide is likely to be absorbed following inhalation of contaminated air. However, data are lacking on the bioavailability of sulfur dioxide following ingestion of contaminated soils and groundwater or foods grown in areas with contaminated air and water. This information would be useful in determining the importance of these routes of exposure.

## 5. POTENTIAL FOR HUMAN EXPOSURE

**Food Chain Bioaccumulation.** No data pertaining to the potential of sulfur dioxide to bioaccumulate or biomagnify in the food chain were identified. This information would be useful in assessing the potential risks associated with the levels of sulfur dioxide in environmental media.

**Exposure Levels in Environmental Media.** Routine monitoring of sulfur dioxide levels in ambient air is currently being performed. However, the monitoring data are insufficient to allow adequate characterization of human exposure to 5- and 10-minute peak levels of sulfur dioxide.

Reliable monitoring data for the levels of sulfur dioxide in contaminated media at hazardous waste sites are needed so that the information obtained on levels of sulfur dioxide in the environment can be used in combination with the known body burdens of sulfur dioxide to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

**Exposure Levels in Humans.** Occupational studies often do not report adequate exposure levels of sulfur dioxide. Additional information is needed on the exposure levels among populations living in the vicinity of hazardous waste sites.

There are several nonspecific biomarkers for sulfur dioxide exposure such as changes in respiratory function or plasma *S*-sulfonate levels. Additional studies to identify specific biomarkers may be useful for the characterization of exposure levels.

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

**Exposures of Children.** Children are primarily exposed to sulfur dioxide through inhalation of polluted air. There are no pathways which are unique to children and further studies on this subject are not necessary. The weight-adjusted intake in children is expected to be greater than adults because children breathe more air per kg of body weight and exercise more frequently. Exercise increases breathing rate, which results in a greater sulfur dioxide dose to the lower respiratory tract. Studies which measure sulfur dioxide intake in children as well as data on respiratory parameters, such as tidal volume and breathing rate, are required to determine actual exposure levels in children. The only way to reduce childhood exposure to sulfur dioxide is by limiting time spent outdoors during periods of high air pollution. Additional research for the prevention of exposure is not required.

## 5. POTENTIAL FOR HUMAN EXPOSURE

Child health data needs relating to susceptibility are discussed in 2.11.2 Identification of Data Needs: Children's Susceptibility.

**Exposure Registries.** No exposure registries for sulfur dioxide were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance 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 this substance.

### 5.8.2 Ongoing Studies

Ongoing studies of the potential for human exposure to sulfur dioxide were not identified.