5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Sulfuric acid is a common chemical that is widely used in industry and is found in consumer products (e.g., car batteries, cleaning products). In the United States sulfuric acid is ranked number one in terms of production volume. Sulfur trioxide is a precursor to the production of sulfuric acid. Oleum (fuming sulfuric acid) is sulfur trioxide absorbed in concentrated sulfuric acid. Sulfur trioxide and sulfuric acid are sometimes released to the environment during production and use. Sulfur dioxide released during the burning of fossil fuels is also a major source of atmospheric sulfuric acid. In the atmosphere, sulfuric acid is generally in the form of small droplets, or it is adsorbed onto small particles. Sulfuric acid leaves the air through dry and wet deposition processes. Because of it’s widespread use, and the widespread release of sulfur dioxide, the potential for human exposure to sulfuric acid is substantial.

Sulfuric acid has been found in at least 47 of the 1,467 current or former EPA National Priorities List (NPL) hazardous waste sites (HazDat 1998). The frequency of these sites within the United States can be seen in Figure 5- 1.

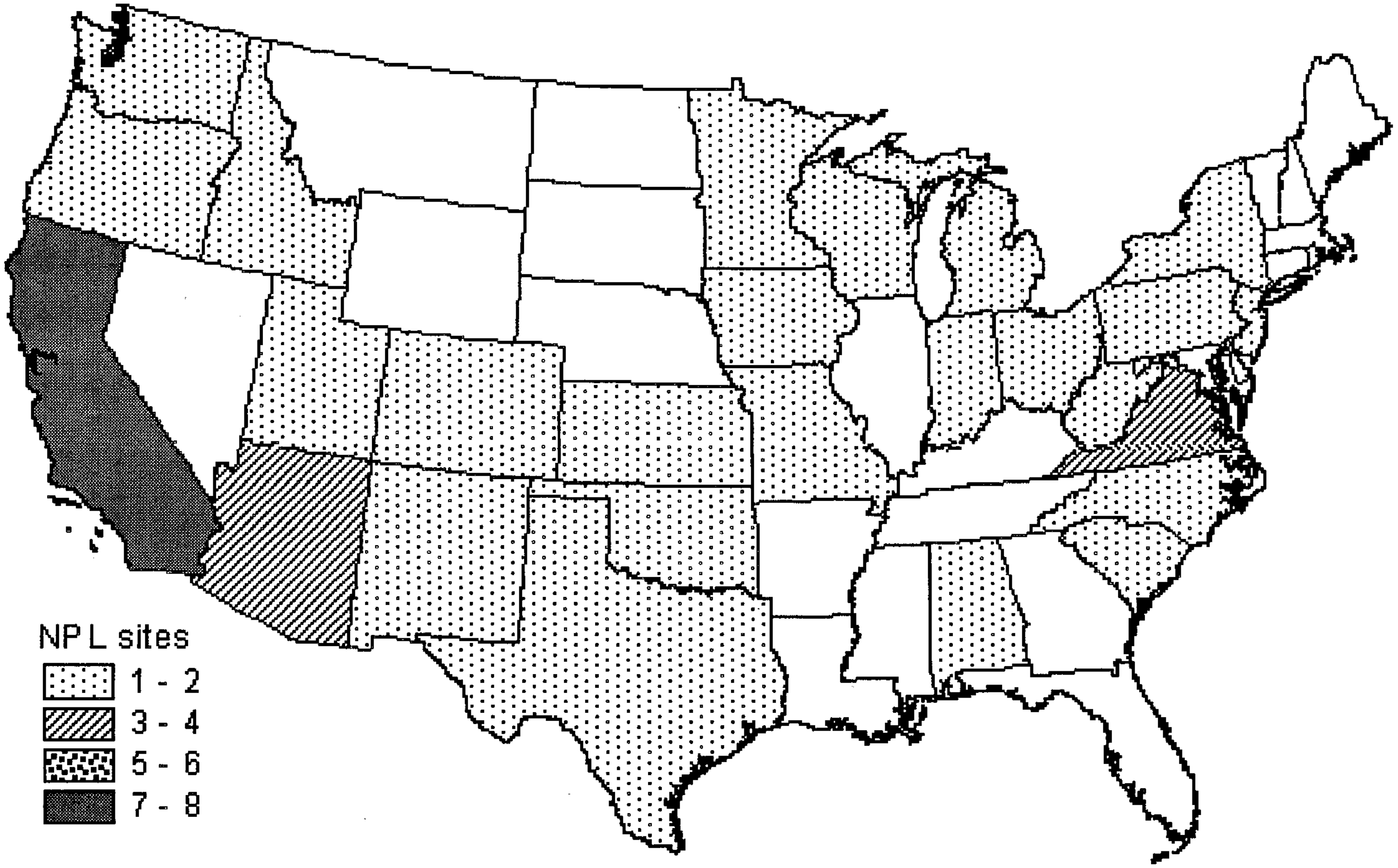
5.2 RELEASES TO THE ENVIRONMENT

According to the TRI, in 1996, releases of sulfuric acid to the environment from 714 large processing facilities totaled 15,077,944 kg (33,246,867 pounds) (TR196 1998). Table 5-l lists ranges of the amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

5.2.1 Air

According to the TRI, in 1996, releases of sulfuric acid to the air from 7 14 large processing facilities totaled 8,929,868 kg (19,690,359 pounds) (TR196 1998). Table 5-l lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Figure 5-1. Frequency of NPL Sites With Sulfuric Acid Contamination



* Derived from HazDat 1998

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Sulfuric Acid

		Total of reported amounts in pounds per year[a]						
State[b]	Number of Facilities	Air[c]	Water	Land	Underground Injection	POTW Transfer	Off-Site Waste Transfer	Total Environment[d]
AL	21	1,243,833	5	12,744	0	25,642	200,794	1,483,018
AR	7	117,396	0	0	0	505	18,681	136,582
AZ	8	436,372	250	0	0	255	238,700	675,577
CA	57	171,677	0	363	0	467,211	175,284	814,535
CO	5	2,309	5	0	0	58,313	0	60,627
CT	6	15,910	0	0	0	750	54,470	71,130
DE	2	66,828	0	0	0	0	0	66,828
FL	29	1,603,280	0	0	0	55,815	2,169,541	3,828,636
GA	29	1,238,427	500	0	0	0	54,450	1,293,377
HI	2	3,267	0	0	0	0	0	3,267
IA	7	16,689	0	0	0	10,000	0	26,689
ID	5	80,253	0	0	0	0	0	80,253
IL	40	526,358	0	0	0	413,743	943,746	1,883,847
IN	23	65,458	0	0	0	23,234	49,324	138,016
KS	5	21,933	0	200	0	250	0	22,383
KY	17	94,706	0	0	0	66,009	1,284	161,999
LA	26	672,624	6	410	0	0	7,934	680,974
MA	16	20,285	0	0	0	29,034	41,606	90,925
MD	7	469,230	0	0	0	1	0	469,231
ME	15	1,504,548	0	0	0	5	305	1,504,858
MI	40	469,353	0	0	0	71,101	2,615,417	3,155,871
MN	4	76,024	0	0	0	13,390	0	89,414
MO	14	75,836	0	20	0	0	0	75,856
MS	8	131,972	0	25,387	0	0	0	157,359
MT	2	44,073	0	0	0	0	0	44,073
NC	24	1,410,940	0	5	0	406,505	69	1,817,519
ND	1	10	0	0	0	0	0	10
NE	1	250	0	0	0	0	0	250
NH	6	275,413	0	0	0	0	600	276,013
NJ	13	34,649	0	0	0	0	136,770	171,419
NM	3	488,755	0	10	0	0	0	488,765
NV	1	14,500	0	0	0	0	0	14,500
NY	21	107,644	0	750	0	6,170	298	114,862
OH	26	1,234,740	0	10	0	0	290,764	1,525,514
OK	7	127,092	0	0	0	49,670	63,636	240,398

Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Sulfuric Acid (continued)

		Total of reported amounts in pounds per year[a]						
State[b]	Number of Facilities	Air[c]	Water	Land	Underground Injection	POTW Transfer	Off-Site Waste Transfer	Total Environment[d]
OR	4	61,813	0	0	0	59	7,700	69,572
PA	37	885,761	250	380	0	6,262	2,354,576	3,247,229
PR	7	10,727	250	3,500	0	13,879	1	28,357
RI	1	17	0	0	0	0	0	17
SC	18	731,393	0	0	0	31,430	2,058,394	2,821,217
TN	22	525,641	5	258	0	27	22,611	548,542
TX	52	717,431	0	804	15,000	16	100,982	834,233
UT	2	74,405	0	0	0	0	0	74,405
VA	12	1,422,153	0	19	0	250	250	1,422,672
VI	1	1,154	0	0	0	0	0	1,154
VT	1	38,000	0	0	0	0	0	38,000
WA	16	383,217	0	0	0	0	2,850	386,067
WI	38	1,847,856	10	7,849	0	148,782	12,373	2,016,870
WV	3	9,508	0	0	0	0	0	9,508
WY	2	118,649	0	0	0	0	0	118,649

Source: TRI96 1998

a Data in TRI are maximum amounts released by each facility

b Post office state abbreviations used

c The sum of fugitive and stack releases are included in releases to air by a given facility

d The sum of all releases of the chemical to air, land, and water, and underground injection wells; and transfers off-site by a given facility

POTW = publicly owned treatment works

Additional data concerning the release of sulfur trioxide or sulfuric acid to the air were not identified. Data regarding emissions of sulfur dioxide, which reacts with water in air to form sulfuric acid, were identified and are summarized below.

Emissions of sulfuric compounds from the earth and the atmosphere are approximately $1{,}100 \times 10^{12}$ g (natural) and 200×10^{12} g (human) (Grzesiak et al. 1997). The largest natural direct source of sulfur dioxide is volcanic eruptions. Major volcanic eruptions which inject sulfur dioxide into the stratosphere are the dominant source of sulfuric acid aerosol in the stratosphere (Hofmann 1990). 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 ($\text{Tg} = 10^{12}$ g; S = sulfur). However, the more well known median estimates were between 9 and 24 Tg S/yr, with the average annual value being ≥ 9 Tg S (DOE 1996). In the stratosphere, at temperatures ranging from -80°C to –45ºC, aqueous spherical droplets are generally composed of 60-80% sulfuric acid. The oceans, which contain about 2.65 mg sulfate/g of water, are also an important source of atmospheric sulfate (Kellogg et al. 1972). 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/yr, according to the Department of Energy (DOE 1996).

In the United States, much of the sulfur dioxide is emitted from electric plants in rural sites. These plants have high stacks and emit plumes with low particle concentrations; these conditions facilitate the production of sulfuric acid in gas and aqueous phases and facilitate the long-range transport of acid aerosols (Spengler et al. 1990). The production of acid aerosols is principally a summertime occurrence because it is driven by photochemistry and the demand for electricity for air conditioning (Spengler et al. 1990).

Aerosols formed from coal combustion have a high concentration of sulfates at the surface (Amdur et al. 1986). This occurs because sulfates condense late, concentrating on the surface. Sulfate concentrations increase with decreasing particle size. Some of the sulfate associated with the aerosols is in the form of sulfuric acid. The amount of sulfuric acid formed is dependent on coal type and the temperature history of particles in the furnace. The differences among coal types are attributed to differences in the ability of the ash to catalyze the oxidation of sulfur dioxide and neutralize the resulting acid. Acid production is highest at a furnace temperature of 1,000 ºK. In an experimental furnace that produced zinc oxide particles, water vapor was shown to be required for the production of sulfuric acid.

The estimated amount of sulfur dioxide emitted in the United States has gone down in recent years (EPA 1995a). In the early 1970s the estimated total emission of sulfur dioxide in the United States was about 28 million metric tons. In 1994 the level had declined to about 18 million metric tons, which is approximately the same amount that was emitted in 1940. The decreases are in part a result of emission controls and a switch to low-sulfur coal by electric utilities. Trends show that in the United States between 1986 and 1995, the national composite SO_2 average decreased 27% and SO_2 emissions decreased 18%. Between 1994 and 1995 SO_2 emissions decreased 13%, and mean national concentrations decreased 17% (EPA 1995a).

When sulfur dioxide emissions were at their maximum, it was estimated that approximately 95% of the sulfur emitted to the atmosphere by anthropogenic operations was in the form of sulfur dioxide (Kellogg et al. 1972). Much of this (about 70%) resulted from the burning of coal. It was estimated that about 93.5% of the sulfur dioxide was produced in the Northern Hemisphere, with only about 6.5% produced in the Southern Hemisphere. Kellogg et al. (1972) concluded that anthropogenic operations were contributing about half as much as nature to the total sulfur burden of the atmosphere.

Atmospheric emissions of sulfur dioxide by 25 countries in Asia east of Afghanistan and Pakistan were estimated based on fuel consumption, sulfur content in fuels, and emission factors for the fuels in each emission category (Kato and Akimoto 1992). From 1975 to 1987 the emission of sulfur dioxide in these countries increased by a factor of 1.59 (from 18.3×10^6 to 29.1×10^6 tons). The six countries of China, India, South Korea, Japan, Thailand, and Taiwan accounted for 92% of the sulfur dioxide released in Asia.

5.2.2 Water

The three major sources of sulfur compounds in bodies of water are rocks, fertilizers, and the atmosphere (Kellogg et al. 1972). The largest contribution is thought to be from the atmosphere. A correlation between sulfate in surface water and sulfate concentrations in precipitation has been observed over a wide range of concentrations (EPA 1985). Background sulfate concentrations in North American lakes are estimated at 20-40 microequivalents/L (μeq/L). In eastern North America where acid deposition occurs, sulfate concentrations are 80-100 μeq/L. Surface water closer to sources of emission has even higher concentrations. For example, lakes near Sudbury, in Ontario, Canada, have concentrations of about 400 μeq/L, and lakes east of the Rhine-Rhone industrial region of Germany can have concentrations of >l,000 μeqL (EPA 1985).

According to the TRI, in 1996, releases of sulfuric acid to water from 7 14 large processing facilities totaled 576 kg (1,271 pounds) (TR196 1998). Table 5-l lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

5.2.3 Soil

According to the TRI, in 1996, releases of sulfuric acid to the soil from 7 14 large processing facilities totaled 23,904 kg (52,709 pounds) (TR196 1998). Table 5-l lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Additional data regarding the release of sulfuric acid to soil were not identified. As indicated, releases to water, rocks, fertilizers, and fallout from the atmosphere would be expected to contribute to the release of sulfuric acid to soil.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Factors that affect the dispersion of sulfur compounds and other air pollutants include the temperature and efflux velocity of the emissions, stack height, topography and the proximity of other buildings, and meteorology. Meteorological conditions that result in temperature inversions can result in the trapping of pollutants, which increases concentrations up to several hundred times the concentrations usually found (WHO 1979).

Sulfates, including sulfuric acid, are removed from the air by both dry and wet deposition processes. Wet deposition processes including rainout (a process that occurs within the clouds) and washout (removal by precipitation below the clouds) contribute to the removal of sulfate from the atmosphere (Kellogg et al. 1972). In the stratosphere, sulfuric acid aerosols have lifetimes of about 14 and 2.4 days at altitudes of 15 and 20 km, respectively (Kellogg et al. 1972). At cloud level, the residence time is about 6 days, with shorter residence times in surface air.

In a study of rain chemistry in southwestern Pennsylvania in August of 1983, Pierson et al. (1987a) concluded that on average about half of the rain sulfate resulted from scavenging of sulfur dioxide, while the rest was from scavenging of aerosol sulfate. The site where the study was completed was about 150 km downwind of the highest density of sulfur dioxide emissions in the United States.

Sulfuric acid is soluble in water. In water, sulfuric acid dissociates, and the sulfate anion may combine with other cations. In soil, the ions from sulfuric acid can adsorb to soil particles or leach into surface water and groundwater. Sulfates can be taken up by plants and be incorporated into the parenchyma of the plant.

A recent study compares dry acid deposition in Florida at two different sites. Sampling was conducted at ground level at one site and above the forest canopy at the other site in order to compare ground level to elevated dry acid deposition. The particulate sulfate levels at both sites were similar, therefore indicating that under these conditions, the deposition is independent of site and elevation (Kim et al. 1997).

5.3.2 Transformation and Degradation

5.3.2.1 Air

Sulfuric acid is formed in the atmosphere from sulfur dioxide. Both gaseous and aqueous phase reactions can occur, with gas phase reactions accounting for only about 5% of the sulfur dioxide oxidized during the summer (Pienaar and Helas 1996). In the process of sulfuric acid formation, sulfur trioxide is formed. After sulfur trioxide is formed, it rapidly reacts with water vapor to form sulfuric acid, so that processes that form sulfur trioxide in moist atmospheres are equivalent to the formation of sulfuric acid (Pienaar and Helas 1996). In the gaseous phase, substances that react with sulfur dioxide resulting in the production of sulfuric acid include O, $HO\bullet$, $HO_2\bullet$, and $CH_2O_3\bullet$. Substances that result in the oxidation of sulfur dioxide in the aqueous phase include ozone and hydrogen peroxide. Metal ions including $CI\text{-}O_4^{2-}$, VO^{2+}, Fe^{2+} , Fe^{3+}, Mn^{2+}, and Ni^{2+} could also directly oxidize SO_3^{2-}, or catalyze SO_3^{2-} oxidation by molecular oxygen. In a study using electron spin resonance, spin trapping, and high-performance liquid chromatography, Shi (1994) found that reactions of SO_3^{2-} with NO_2^- also generate $SO_3^\bullet$ radicals. The major reactions that form sulfuric acid from sulfur dioxide require light. Therefore, levels of sulfuric acid in the atmosphere show both seasonal and diurnal variations.

The production of sulfuric acid from sulfur dioxide can become limited if the concentrations of oxidants are less than the concentrations of sulfur dioxide. Oxidant limitations of the formation of sulfuric acid were shown in a study of sulfur dioxide and hydrogen peroxide concentrations over Columbus, Ohio; the study authors suggested that similar conditions exist over a large area of the eastern United States (Kleinman and Daum 199 1). A deficiency of hydrogen peroxide relative to sulfur dioxide was also shown in a study completed at Whiteface Mountain, NY (Dutkiewicz et al. 1995). These results suggest that there would be a nonlinear relationship between sulfur dioxide emissions and downwind acid precipitation in the northeastern United States where aqueous-phase oxidation by hydrogen peroxide is the principal mechanism for forming sulfuric acid. The aqueous oxidation of sulfur dioxide to sulfuric acid in precipitation has been estimated to account for 50-80% of the sulfuric acid found in precipitation (Fung et al. 1991).

Acid aerosols react with gaseous ammonia to form partially neutralized ammonium salts. If ammonia is present, sulfuric acid will react to form ammonium sulfate, which is considered neutral for most practical purposes (Wyzga and Folinsbee 1995). The intermediate reaction products ammonium bisulfate and ammonium hemisulfate, which are fairly stable and may be present in abundance, are acidic. Aerosol neutralization is dependent on the rate of sulfur dioxide oxidation to sulfate and on the ambient concentrations of ammonia (Lui et al. 1996). Among three sites in Pennsylvania with varying degrees of urbanization, $H^+$was the lowest and ammonia was the highest in the most urbanized area. Concentrations of both $H^+$and sulfate were higher during the daytime, probably a result of daytime conversion of sulfur dioxide to sulfate. Diurnal variations in ammonia concentrations were not observed.

The effect of wind speed on the ammonia neutralization of sulfuric acid was studied under chamber conditions (Clark et al. 1995). During exposure to an average sulfate ion concentration of 0.105 mg/m^3, about 25% of the breathing-zone acid was neutralized without wind, while 10% was neutralized with a wind of 4 or 16 km/hour.

In air, submicron-sized sulfuric acid aerosol droplets rapidly take up water from the atmosphere. For example, the growth of a sulfuric acid droplet (original sulfuric acid concentration of 98% and size of 1 pm) was complete in 0.01 second after exposure to an atmosphere of relative humidity 50% at 20°C (Carabine and Maddock 1976).

5.3.2.2 Water

In water, sulfuric acid dissociates. The sulfate anion may associate with other cations including calcium, magnesium, and aluminum. Sulfur that is in water may be oxidized to sulfuric acid by sulfur bacteria (Thiobacilli) that use sulfur to obtain energy for growth (Takeuchi and Suzuki 1994). Sulfate in water can also be reduced. Because sulfur dioxide and sulfate are transformed through similar pathways in water, the effect of sulfur on aquatic systems is not dependent on the chemical or physical form of deposition (wet or dry) (EPA 1985).

In the surface layer of the ocean the sulfate anion may be formed from dissolved sulfur dioxide, which is transformed to sulfurous acid (H,SO,) and subsequently oxidized. Because of the relative lack of salt in freshwater, the oxidation of sulfur dioxide to sulfate is less likely to occur in freshwater. In the depths of the ocean, sulfate is reduced to sulfur dioxide, sulfur, and hydrogen sulfide by bacteria (Kellogg et al. 1972).

5.3.2.3 Sediment and Soil

The ions (sulfate, hydrogen) can adsorb to soil particles or be converted to gases (EPA 1985). Anaerobic bacteria in sediments and soil can reduce sulfate to sulfur and hydrogen sulfide (Kellogg et al. 1972).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

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

5.4.1 Air

Air monitoring results are often reported in terms of hydrogen ion or sulfate concentrations, or sulfuric acid equivalents, rather than sulfuric acid concentrations. The local concentration of acidity is dependent on the balance between acids and bases and is difficult to estimate using meteorological dispersion models (Lipfert et al. 1989). Peak sulfuric acid concentrations that have been reported include 240 $\mu g / m^3$ in the Los Angeles area in 1950, an hourly average of 678 µg /rn^3 in London during an episode in 1962, and an hourly average of 50 µg / m^3 in Ontario during the summer of 1986 (Amdur 1989b).

The highest concentrations of aerosol acidity are found in the eastern United States and southern Ontario, Canada. This results because of the major power plants in the Ohio River Valley region and the ability of the acid precursors to be transported. (Spengler et al. 1990). Usually, acid aerosol concentrations are higher during the day than at night and higher during the summer. Acid concentrations may be higher in rural areas because of higher ammonia emissions that result in greater neutralization of the acid. Arithmetic annual average sulfate concentrations measured from 1964 to 1968 were 13.5 µg/m^3 for urban sites in the eastern United States and 6.4 µg/m^3 for urban sites in the western United States (Altshuller 1973). At eastern sites, 7% of the annual averages were above 20 µg/m^{3}g while no annual averages were above 20 µg/m^3 at western sites. The minimum detectable concentration of sulfate during this study period was 0.6 µg/m^3. The average ratio of sulfur dioxide to sulfate was 4.7: 1, witb a ratio of 4.9: 1 at eastern urban sites, and a ratio of 3.4: 1 for western urban sites (Altshuller 1973). A review of studies of the measurement of sulfuric acid or hydrogen ion (as sulfuric acid) in the United States from 1974 to 1986 indicated that the concentrations were generally below 5 µg / m^3 (Lioy and Waldman 1989). The highest concentration reported in these studies was a 1 -hour average of 41 µg /m^3 in 1984 at a site in St. Louis, MO. Lioy and Waldman (1989) cautioned that periods of high acid do not necessarily occur at the same time as periods of high atmospheric sulfate. For example, in a study of hydrogen ion and sulfuric acid, the median level of sulfuric acid was about 15% of the median level of hydrogen ion (Lipfert et al. 1989).

Outdoor, indoor, and personal sulfate, hydrogen ion, and ammonia levels were measured in State College, PA (Suh et al. 1993). The samples were collected over 12-hour daytime periods. The indoor samples were taken from 47 homes; 21 had air conditioning. As indicated in Table 5-2, the outdoor concentrations of sulfate and hydrogen ion were greater than the indoor concentrations, while the personal values were close to the results from indoor measurements. Ammonia levels were higher inside than outside, and personal ammonia monitors indicated even higher levels of exposure.

Daily distributions of acid aerosol concentrations were examined in Kingston, TN, and St. Louis, MO, in 1986, and in Steubenville, OH, and Portage, WI, in 1987 (Spengler et al. 1989). Elevated acid aerosol concentrations occurred more frequently in the summer months. Approximately 50% of the days, acid aerosol concentrations expressed as equivalents of sulfuric acid in µg/m^3 were about 1,0.2,0.6, and 0.1 in

TABLE 5-2. Outdoor, Indoor, and Personal Concentrations of Sulfate, Hydrogen Ion, and Ammonia[a]

Sample type	Sample size	Geometric mean (nmol/m^3)	Geometric standard deviation
Sulfate			
Outdoor	76	90.98	2.45
Indoor	214	69.13	2.62
Personal	209	71.53	2.40
Hydrogen ion			
Outdoor	75	72.39	2.87
Indoor	168	9.10	3.51
Personal	174	18.39	3.03
Ammonia			
Outdoor	78	2.94	0.43
Indoor	214	19.86	2.20
Personal	200	28.05	2.08

[a] Modified from Suh et al. 1993

Kingston, St. Louis, Steubenville, and Portage, respectively. The maximum concentrations in μg/ m^3 were about 10, 3.5, 10.5, and 2.5 in Kingston, St. Louis, Steubenville, and Portage, respectively.

Measurements of sulfuric acid aerosols in the stratosphere over Laramie, WY, indicate increases of about 5±52% per year from 1979 to 1990 (Hofmann 1990). It is not yet known whether this increase is a result of natural or anthropogenic sources. Above the Atlantic Ocean, sulfate concentrations of 2-5 μg / m^3 have been reported (Kellogg et al. 1972).

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

Acidic acid aerosols were measured in Erfurt in east Germany and Sokolov in the Czech Republic during December 1990 until June 1992 (Cyrys et al. 1995). Concentrations of sulfur dioxide, sulfate, and H^+ (as H_2SO_4) in μg/ m^3 averaged 84.6,9.6, and 0.3, respectively, in Erfurt, and 62.1, 8.8, and 0.4, respectively, in Sokolov. These results and other studies reviewed by the study authors indicate that acidity in Europe is generally lower than in North America. The investigators noted that in eastern Europe sulfur dioxide and ammonia are emitted at the same height so that acidic sulfate will be neutralized. In the European cities, days with noticeable acidity were more prevalent during the winter than during the summer.

Measurements of acid aerosols at 8 sites in the Netherlands from October 1987 to April 1990 showed concentrations occasionally in excess of 1 μg / m^3, but never exceeding 10 μg/m^3 (Hoek et al. 1996).

The size range of acid droplets collected in the environment is large. Acid droplets can be found on all stages of a cascade impactor (0.5-23 μm). The larger droplets often appear to be associated with solid particles (Waller 1963). The largest number of droplets is usually collected at relative humidities of about 90%.

5.4.2 Water

The levels of sulfate in the water are highly dependent on nearby emissions of sulfur containing compounds which can be converted to sulfuric acid. Background sulfate concentrations in North American lakes are estimated at 20-40 μeq/L (EPA 1985). In eastern North America where acid deposition occurs, sulfate concentrations are 80-100 μeq/L. Surface water closer to sources of emission has even higher concentrations. For example, lakes near Sudbury in Ontario, Canada, have concentrations of about 400 μeq/L. In Europe, lakes east of the Rhine-Rhone industriaP region of Germany can have concentrations of >1 ,000 μeqL (EPA 1985).

5.4.3 Sediment and Soil

Data regarding the levels of sulfuric acid in sediment and soil were not identified.

5.4.4 Other Environmental Media

Data regarding the levels of sulfuric acid in other environmental media were not identified.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Occupational exposures to sulfuric acid mists (particle size measurements not available) in pickling, electroplating, and other acid treatment of metals are frequently above 0.5 mg/ m^3, with lower concentrations generally found in the production of phosphate fertilizer and in the manufacture of lead-acid batteries (IARC 1992). Sulfuric acid exposure also occurs when it is manufactured and when isopropanol, synthetic ethanol, and detergents are produced. Other industries where there is potential exposure to sulfuric acid include building and construction, electric and electronic equipment, food products, health services, instruments, leather, oil and gas extraction, petroleum and coal products, photography shops, printing and publishing, paper and allied products, rubber and plastic products, steel, and textile products (IARC 1992).

The National Occupational Exposure Survey (NOES), conducted by NIOSH from 1981 to 1983, estimated that 56,103 and 775,348 U.S. workers may be exposed to sulfur trioxide and sulfuric acid, respectively (NOES 1990). The NOES database does not contain information regarding the frequency, concentration, or duration of exposure; the survey provides only estimates of workers potentially exposed to chemicals in the workplace, and is based on sample populations only.

At five lead-acid battery plants in the United States, the average sulfuric acid concentration was 0.18 mg/ m^3 with a range of nondetectable (detection limit not stated) to 1.7 mg/ m^3 (Jones and Gamble 1984). The MMAD of the sulfuric acid mist was about 5 pm. Low levels of stibine, amine, and arsenic in particulate form were also detected. The average lead concentration was 0.72 mg/ m^3. Workers at two battery manufacturing plants in Egypt were exposed to sulfuric acid vapor at concentrations of 12.55-35.02 mg/ m^3 (El-Sadik et al. 1972). The particle sizes were not provided.

A study of kerosene heaters indicates that they can be a source of acidic aerosols in indoor air. The emission rate for acid aerosols calculated as sulfuric acid ranged from 0.6 to 63.1 µg /g of fuel (Leaderer et al. 1990). The particles produced by the 4 heaters used in this study were less than 2.5 ym in diameter. The investigators noted that the heater that produced the highest levels of acid aerosols “showed evidence of considerable use and may have been maltuned.”

The following three accidental exposure cases examine the effects of a single exposure to H,SO,. A worker was exposed to fumes caused by the addition of water to oleum, and he was hospitalized and treated for bums and respiratory problems. Six months later, the worker was readmitted for bronchiectasis and diffuse intersitital fibrosis. This case supports the idea that one single exposure to sulfuric acid can cause progressive lung damage (Griffiths 1996). A man suffered chemical pneumonitis, infection, and a lung abscess when a 95% sulfuric acid mixture was released from a drain. A later chest X-ray revealed no permanent damage to the lungs (Griffiths 1996). Nine people suffered symptoms ranging from chest pain to nasal irritation following a 2 hour exposure to sulfur trioxide. All of the patients were treated and released within six hours (Griffiths 1996).

Measurements of personal exposure to hydrogen ion and sulfate were completed for 24 days during the summer of 1988 in Boston, MA, and were compared to nearby outdoor stationary site sampling data (Brauer et al. 1989). The total number of persons involved in this study was not stated, but there were a total of 3 1 indoor 24-hour sulfate samples and a total of 13 indoor 24-hour hydrogen ion samples. Personal measurements of sulfate were similar to those at the outdoor site. Personal measurements of hydrogen ion were lower than the outdoor samples as a result of neutralization of acidic particles and of the incomplete penetration into indoor locations. Similar results were observed for hydrogen ion and sulfate when personal monitors were used by 24 children living in Uniontown, PA (Suh et al. 1992). Air conditioning was found to reduce indoor hydrogen ion concentrations, a result of increased ammonia levels resulting from reduced air exchange rates.

Exposure models for sulfate and hydrogen ion have been developed to provide better predictions of exposure relative to outdoor air concentrations of sulfate and hydrogen ion (Suh et al. 1993). These models were developed and validated using air monitoring data and data from children living in rural and semi-rural environments (Uniontown and State College, PA). Because the models were developed in specific environments, the authors cautioned that the models were only applicable to those environments, and that before being used in an urban setting, the model should be validated with urban data. When the sulfate model was compared to actual personal exposure data, it was found that sulfate exposure could be adequately predicted by the outdoor concentration, activity of the person, and use of air conditioning. This model accounted for about 9 1% of the variability in personal sulfate exposure. The hydrogen ion model included a neutralization term and was better at predicting personal exposure when indoor air concentrations of hydrogen ion and personal ammonia levels were also included. With all the information included in the model, the model accounted for 63% of the variability in personal hydrogen ion exposure. When outdoor concentrations and activity data were used in the model, with the assumption that indoor air concentrations were zero, the model explained only 47% of the variability in measured personal hydrogen ion exposure. Because of the importance of personal ammonia levels on predicting hydrogen ion exposure, and because of similar difficulties in measuring personal ammonia and hydrogen ion concentrations, the study authors suggest that direct measurement of personal hydrogen ion exposure may be the only method to accurately determine personal hydrogen ion exposure.

The RASP model was developed to study the release of sulfur trioxide vapors from a sulfur trioxide pool or oleum. The model is dependent on release rate, minimum pool depth, wind speed, maximum pool radius, water film thickness, duration of spill, and duration of release (Griffiths 1996).

The TOEM model calculates wind drive release rates from sulfur trioxide or oleum spills. The model is dependent on wind speed, quantity spilt, release rate, maximum pool radius, spill duration, and total time of release (Griffiths 1996).

The relationship between hydrogen ion, sulfate, ozone, and population density has been examined using measurements from across the United States and Canada (Ozkaynak et al. 1996). Significant site-specific and regional relationships between hydrogen ion and sulfate and population density were observed. The relationships were stronger in the eastern United States compared to the west or midwest, where local pollution, agricultural activities, and industrial sources of ammonia had a greater impact on the lower hydrogen ion levels. The relationships were also stronger during the summer compared to the winter. The study authors concluded that reasonable estimates of hydrogen ion levels could be made using sulfate data and data on local population density.

Exposure to sulfuric acid and oleum can also occur through accidental releases. Among states reporting accidental events during the time period 1990-1996 (5 states 1990-1991, 9 states 1992-1994, 14 states 1995-1996) 905 events occurred that involved only sulfuric acid and oleum (3 oleum releases), and 173 events occurred that involved mixtures or multi-chemical releases that included sulfuric acid or oleum (HSEES 1997). The 14 states that are presently participating are Alabama, Colorado, Iowa, Minnesota, Missouri, Mississippi, New Hampshire, New York, North Carolina, Oregon, Rhode Island, Texas, Washington, and Wisconsin. The majority of the releases occurred at a fixed facility rather than a result of a transportation accident. For events with sulfuric acid or oleum alone, 78.7% of the events occurred at fixed facilities, while 81.5% of the events with mixtures including sulfuric acid or oleum occurred at fixed facilities. A spill was the most frequent type of release (85.1% sulfuric acid or oleum only; 63.6% mixture including sulfuric acid or oleum). Among the events in which only sulfuric acid and oleum were released, 53 required evacuation (information not available for 39 events), there was 1 death, and a total of 203 victims. Chemical bums (38.5%), respiratory irritation (21.6%), and eye irritation (15.4%) were the most frequently reported effects following these releases. Among the mixture or multi-chemical releases that included sulfuric acid or oleum, 40 required evacuation (information not available for 3 events), there were 3 deaths, and a total of 322 victims. The most frequently reported effects following the release of mixtures were respiratory irritation (56.5%), eye irritation (17.8%), and nausea and vomiting (5.1%).

In Richmond, CA, 1993, a 12,000 gallon rail tanker leaked oleum into the environment. The release formed a 330 m high by 13 km wide cloud in a highly populated area, and between 2,000 and 22,000 people were treated for effects (Griffiths 1996).

DuPont conducted a spill test in 1992 that tested water chemicals, dry chemicals, and commercial foams on small oleum spills in Nevada. The test found which products treated the spill the best and in the least time. The foam products treated the spill in half the time of the water and dry chemicals. Foam products also kept the temperature of acid in the pool down (Griffiths 1996).

The general population can also be exposed to sulfuric acid through the use of lead-acid batteries (including car batteries) and cleaners (especially toilet bowl cleaners that contain sodium bisulfate, which produces sulfuric acid when it contacts water). People can also be exposed to sulfuric acid when they cut onions. Cutting onions releases the compound propanethiol *S*-oxide which reacts with water in the eyes to form sulfuric acid, which causes the eyes to water (Hillman 1989).

5.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans and briefly considers potential preconception 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 humans 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 trioxide gas is an intermediate used in the manufacture of chemicals such as sulfuric acid. With the exception of large accidental releases from chemical plants, exposure of children to sulfur trioxide is unlikely. Because small amounts of sulfur trioxide rapidly combine with moisture in air to produce sulfuric acid, children living near industries that utilize sulfur trioxide may be exposed to increased levels of sulfuric acid in air. Sulfuric acid is also present in air because it forms upon reaction with sulfur dioxide and water. Therefore, increased exposure to sulfuric acid aerosols in air is expected for children living in areas in which large amounts of sulfur dioxide are released by industries, such as electrical, metal processing, and paper manufacturing. Decreased respiratory performance in asthmatics and reduced mucocilliary clearance in healthy individuals are the primary effects associated with exposure to sulfuric acid aerosols. Concentrations as low as 0.07 mg/ m^3 (MMAD 0.7 1 μm) have produced transient reductions in the pulmonary function of exercising asthmatic adolescents in chamber studies (Hanley et al. 1992).

Sulfuric acid is used in household products, such as drain and toilet bowl cleaners and car batteries. Children are most likely to be exposed to high concentrations of sulfuric acid through ingestion, eye contact, or skin contact. There are no exposure pathways that are unique to children. However, young children are more prone to accidents involving ingestion or eye and skin contact with cleaners containing sulfuric acid. Eye and skin exposure in teenagers is possible through the use of sulfuric acid in chemistry lab courses in high schools. Occupational exposure to sulfuric acid is also possible for teenagers who have jobs which require them to use acid cleaners. Teenagers who have jobs in automotive repair could also be exposed to sulfuric acid from car batteries. Depending on the concentration of the sulfuric acid solution, direct contact with tissues can result in severe chemical burns and death. There is no clear evidence available which indicates the minimum concentration that will cause chemical burns in tissues.

Significant exposures of children are not anticipated through diet, structural building materials, or the clothing, skin, or breath of occupationally exposed parents.

There are no studies in which the levels of sulfuric acid were measured in the blood of children, in maternal reproductive organs during pregnancy, or in breast milk. Because sulfuric acid is a direct acting toxicant, which exerts its effect at the point of contact, significant absorption and distribution throughout the body is unlikely. Upon inhalation exposure, the weight-adjusted intake of sulfuric acid in the respiratory system is expected to be greater in children because they bream more air per kilogram of body weight than adults. I n addition, a model has indicated that total deposition of sulfuric acid in the respiratory tract is greater in children than adults (Martonen and Zhang 1993). Numerous factors determine pulmonary exposure to sulfuric acid aerosols including the aerosol size, relative humidity, and physiological breathing factors, such as rate or percentage of time breathing through the nose or mouth. Additional research involving these factors is required before the weight adjusted intake of sulfuric acid can be determined.

In vitro experiments have demonstrated that sulfuric acid can induce chromosomal aberrations (Cipollaro et al. 1986; Morita et al. 1989; Zura and Grant 1981). However, it is unlikely that sulfuric acid would reach germ cells and there should be no concern regarding exposure of parental germ cells. Exposure of fetuses is also unlikely, and developmental studies have demonstrated a lack of adverse effects (Murray et al. 1979). Refer to section 2.6 for a more detailed discussion about genotoxicity and developmental effects.

Pharmacokinetics studies which examine whether sulfuric acid is stored in maternal tissues are not available. Because absorption of significant amounts of sulfuric acid is not expected, storage in maternal tissue and subsequent release during pregnancy or lactation is very unlikely.

Reduction of sulfuric acid exposure in children primarily involves preventing direct contact with tissues. Following the use of sulfuric acid cleaners, surfaces and surrounding areas should be thoroughly rinsed. Exposures in small children can be avoided by storing sulfuric acid cleaners in original, labeled, intact containers within locked cabinets. If teenagers must use sulfuric acid or sulfuric acid-based cleaners, exposure to the eyes and skin can be prevented with the use of eye goggles and chemical resistant gloves. Eye protection is also recommended for teenagers working with car batteries. If sulfuric acid contacts the skin or eyes, the affected area should be immediately flushed with water. A poison control center must be immediately contacted in cases where the acid is ingested. Inhalation exposure to sulfuric acid pollution can be reduced in children by limiting the time spent outdoors, especially during periods of high pollution.

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to persons working in industries where sulfuric acid is used, persons living in industrialized areas, especially those living near electric power plants, may be exposed to higher levels of sulfuric acid. Persons who frequently work with car batteries and other lead-acid batteries may also be exposed to higher levels of sulfuric acid. Toilet bowl cleaners often contain sodium bisulfate which produces sulfuric acid when it contacts water. Therefore, misuse of these products may result in higher-than-normal exposure to sulfuric acid.

Sulfuric acid levels are generally lower indoors than outdoors. Therefore, persons who spend most of their time outside may be exposed to higher levels. This may be especially true for persons who engage in considerable outdoor physical activity. Physical activity not only increases breathing rate but increases the amount of oral breathing which would increase the amount of sulfuric acid aerosols reaching the lungs. Although increased exposure is expected in persons who spend a great deal of time outside, it does not necessarily mean that those individuals will be exposed to harmful levels of sulfuric acid mists. Unacceptable exposure levels are potentially possible in persons who are outdoors for extended periods during episodes of high pollution.

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 trioxide/sulfuric acid 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 trioxide and sulfuric acid.

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. The physical and chemical properties of sulfur trioxide, sulfuric acid, and fuming sulfuric acid are generally well characterized (HSDB 1998; NIOSH 1994b). Further research on the aerosol size of sulfuric acid at occupational settings and in the environment is needed.

Production, Import/Export, Use, Release, and Disposal. According to the Emergency Planning and Community Right-to-Know Act of 1986,42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1996, became available in May of 1998. This database is updated yearly and should provide a list of industrial production facilities and emissions. However, the TRI data is not exhaustive because certain types of facilities are not required to report releases. Additional information would be useful about quantities and frequencies of releases from exempt facilities, especially those that may release sulfuric acid or sulfur trioxide levels resulting in 5- and 10-minute peak exposures to high concentrations.

Environmental Fate. Once sulfuric acid enters the environment, the sulfur enters the natural sulfur cycle which is well defined (Kellogg et al. 1972). Additional research regarding the environmental fate of sulfuric acid does not appear to be necessary at this time.

Bioavailability from Environmental Media. As part of the natural sulfur cycle, sulfur compounds can be taken up by plants. The adsorption of sulfuric acid on small particles increases the toxicity of sulfuric acid (Amdur 1989b). This effect is thought to result, at least in part, from a change in the deposition of sulfuric acid in the respiratory tract, not an increase in bioavaila0ility. Because sulfuric acid is a direct-acting toxicant, rather than a substance that causes toxic effects after being absorbed into the blood stream, bioavailability from different media is not an important issue for sulfur trioxide and sulfuric acid.

Food Chain Bioaccumulation. Sulfur is an important constituent of normal biomolecules. Food chain bioaccumulation is not an important issue for either sulfur trioxide or sulfuric acid.

Exposure Levels in Environmental Media. Air is the environmental media most relevant to human exposure to sulfuric acid. Air monitoring results are often reported in terms of hydrogen ion or sulfate concentrations, or sulfuric acid equivalents, rather than sulfuric acid concentrations. Additional data concerning the aerosol size of sulfuric acid in air is needed.

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

Exposure Levels in Humans. Models for personal sulfate and hydrogen ion exposure have been developed (Suh et al. 1993). Improvement in personal ammonia monitoring would improve the ability to predict personal hydrogen ion exposure. This information is necessary for assessing the need to conduct health studies on these populations.

There is no specific biomarker for human exposure to sulfuric acid. The only potential biomarker may be measurement of pH in saliva. Because saliva has some buffering capacity, decreases in saliva pH would only be apparent at relatively high-level sulfuric acid exposures, and decreases in pH can occur following exposure to other acids.

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

Exposures of Children. Children are exposed to sulfuric acid through ingestion or direct contact with specific cleaners or battery acid. Inhalation of sulfuric acid air pollution is another source of exposure. There are no exposure pathways which are unique to children and studies to address this issue are not required. Exposure through any route is not likely to result in significant absorption and distribution. Therefore, studies regarding body burden in children are not required. Reduction of exposure involves preventing direct contact of solutions with tissues or limiting time spent outdoors during periods of high air pollution to decrease the quantity inhaled. Research in exposure reduction is not required. Deposition and distribution of sulfuric acid aerosols within the respiratory tract are likely to differ between adults and children due to differences in respiratory performance. Therefore, studies in the pulmonary weight-adjusted intake of sulfuric acid and distribution within the respiratory system in children would be useful.

Exposure Registries. No exposure registries for sulfuric acid 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

The production of sulfuric acid by various reactions in the upper troposphere and lower stratosphere is being studied further by Somorjai and Johnston (FEDRIP 1996). Tabatabai is studying wet deposition, including sulfuric acid deposition in central Iowa (FEDRIP 1996). Xiong and coworkers at the New York University Medical Center in Tuxedo, New York, are studying the effect of organic films on the reactivity and hygroscopicity of sulfuric acid aerosols (Xiong et al. 1997).