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5.1 OVERVIEW

Antimony and its compounds are naturally present in the earth's crust. Releases to the environment occur from natural discharges such as windblown dust, volcanic eruption, sea spray, forest fires, and biogenic sources, as well as from anthropogenic activities. Therefore, it is important to consider the background levels that are due to natural sources and distinguish these from higher levels that may result from anthropogenic activities. According to the SARA Section 313 TRI, an estimated total of 3,061,036 pounds of antimony were released to the environment from manufacturing, processing, and antimony-using facilities in the United States in 1987 (TRI 1989). Of these releases, 92.9% was to land, 4.4% was to air, 2.0% was to water, and 0.6% was to underground injection. Table 5-1 lists releases of antimony to air, water, and land from these facilities. Companies above a minimum size are required to report if they produce, import, or process over 75,000 pounds of antimony and its compounds or use in excess of 10,000 pounds. The quality of the TRI data must be viewed with caution since the 1987 data represent first-time, incomplete reporting of estimated releases from these facilities. Not all sources of chemical waste are included, and not all facilities that should have reported have done so.

Most antimony released to the atmosphere from anthropogenic sources results from metal smelting and refining, coal-fired power plants, and refuse incineration. Since antimony is a fairly volatile metal, it will volatilize during combustion processes and subsequently condense on suspended particulate matter that is predominantly less than 1 μm in size. Such fine particles are less efficiently trapped by pollution control devices than are larger particles. In the atmosphere, they tend to settle out slowly; they are also removed by dry and wet deposition. A model that relates particle size to volatility estimates average atmospheric half-lives of 1.9 and 3.2 days for antimony and antimony trioxide, respectively (Mueller 1985). Submicron particles may have atmospheric half-lives as long as 30 days (Schroeder et al. 1987). The long atmospheric half-life and monitoring data indicate that antimony can be transported far from its source (Dutkiewicz et al. 1987; Hillamo et al. 1988). Antimony concentrations in air particulate matter in remote, rural, and U.S. urban areas are 0.00045-1.19, 0.6-7, and 0.5-171 ng/m^3, respectively (Austin and Millward 1988; Schroeder et al. 1987).

The speciation and physicochemical state of antimony are important to its behavior in the environment and availability to biota. For example, the antimony incorporated in mineral lattices is inert and unlikely to be bioavailable. Most analytical methods for antimony do not distinguish the form of antimony. While the total amount of antimony may be known, the nature of the antimony compounds and whether they are adsorbed to other material are not. This information, which is critical in determining antimony's lability and availability, is apt to be site-specific.

TABLE 5-1. Releases to the Environment from Facilities That
Manufacture, Process, or Use Antimony and Compounds[a]

State[c]	No. of facil- ities	Range of reported amounts released in thousands of pounds[b]						
		Air	Underground injection	Water	Land	Total Environment[d]	POTW[e] transfer	Off-site waste transfer
AL	5	0-0	0-0	0-3	0-29	0-30	0-0	0-16
AR	3	0-0	0-0	0-0	0-0	0-0	0-0	0-8
AZ	3	0-14	0-0	0-0	0-1,562	0-1,576	0-0	0-0
CA	16	0-1	0-0	0-0	0-0	0-1	0-5	0-52
CO	2	0-1	0-0	0-0	0-0	0-1	0-0	1-37
CT	5	0-0	0-0	0-0	0-0	0-0	0-0	0-2
DE	1	0-0	0-0	0-0	0-0	0-0	0-0	0-0
FL	3	0-0	0-0	0-0	0-0	0-0	0-0	0-1
GA	8	0-1	0-0	0-0	0-0	0-1	0-1	0-22
ID	3	0-1	0-0	0-3	0-140	0-144	0-0	0-0
IL	11	0-1	0-1	0-0	0-0	0-1	0-0	0-5
IN	12	0-2	0-0	0-0	0-2	0-2	0-32	0-122
KS	4	0-0	0-0	0-0	0-0	0-0	0-0	0-9
KY	12	0-2	0-0	0-1	0-0	0-2	0-0	0-112
LA	8	0-1	0-9	0-26	0-10	0-26	0-0	0-22
MA	10	0-1	0-0	0-0	0-0	0-1	0-0	0-9
MD	4	0-7	0-0	0-0	0-0	0-7	0-3	0-7
MI	7	0-1	0-0	0-1	0-0	0-2	0-0	0-13
MN	5	0-0	0-0	0-0	0-20	0-20	0-0	0-12
MO	8	0-0	0-0	0-0	0-11	0-12	0-0	0-10
MS	5	0-0	0-0	0-0	0-0	0-0	0-0	0-25
MT	1	3-3	0-0	0-0	224-224	226-226	0-0	0-0
NC	9	0-0	0-0	0-0	0-1	0-1	0-0	0-14
NE	3	0-30	0-0	0-0	0-1	0-31	0-5	0-112
NJ	22	0-1	0-0	0-0	0-0	0-1	0-0	0-10
NM	1	0-0	0-0	0-0	0-0	0-0	0-0	0-0
NY	8	0-0	0-0	0-0	0-0	0-0	0-0	0-56
OH	34	0-9	0-0	0-0	0-13	0-13	0-13	0-35
OK	4	0-0	0-0	0-0	0-0	0-0	0-3	0-1
OR	1	0-0	0-0	0-0	0-0	0-0	0-0	0-0
PA	21	0-1	0-0	0-1	0-0	0-1	0-0	0-25
RI	2	0-0	0-0	0-0	0-0	0-1	0-0	0-0
SC	12	0-1	0-0	0-1	0-1	0-1	0-16	0-38
TN	7	0-0	0-0	0-0	0-33	0-33	0-3	0-47
TX	24	0-8	0-8	0-5	0-470	0-475	0-2	0-83
VA	4	0-1	0-0	0-0	0-0	0-1	0-0	0-12

TABLE 5-1 (Continued)

State[c]	No. of facil- ities	Range of reported amounts released in thousands of pounds[b]						
		Air	Underground injection	Water	Land	Total Environment[d]	POTW[e] transfer	Off-site waste transfer
VT	4	0-0	0-0	0-0	0-0	0-0	0-0	0-0
WA	2	0-0	0-0	0-9	0-54	0-63	0-0	0-13
WI	9	0-1	0-0	0-1	0-31	0-33	0-0	0-89
WV	2	0-0	0-0	0-0	0-0	0-0	0-0	0-10

[a]TRI 1989
[b]Data in TRI are estimated annual releases by each facility.
[c]Post office state abbreviation
[d]The sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility.
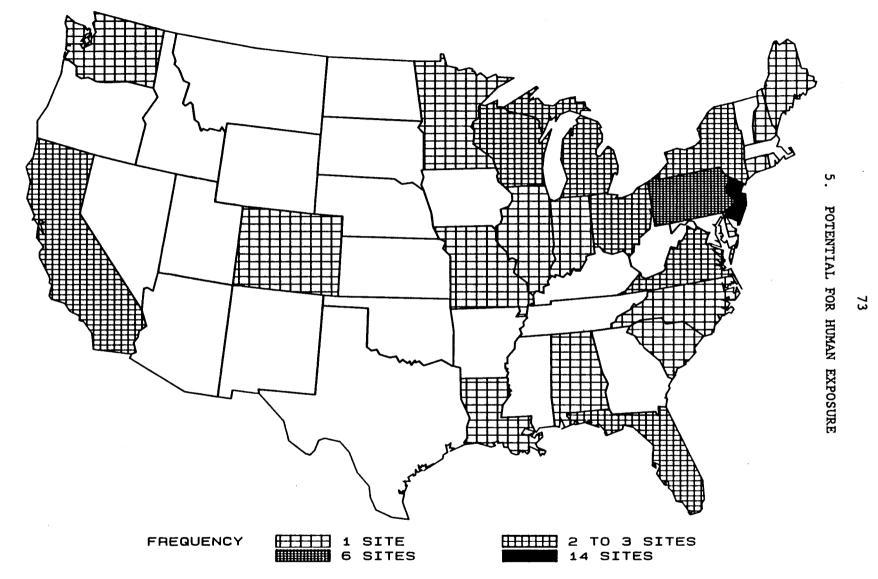[e]publicly owned treatment works

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Antimony occurs in soil and rock in very low concentrations; the range of concentration in soil ranges from less than 1 to 8.8 ppm, with a mean of 0.48 ppm (Shacklette and Boerngen 1984). This is the third lowest of 50 elements surveyed by the U.S. Geological Survey. The forms of antimony in various soils and the transformations between these forms is poorly understood. The available data indicate that the lability of antimony may vary considerably according to its environment. In one study, three-quarters of the soil near a smelter site was in a residual (extractible with aqua regia) fraction (Ainsworth 1988). While the concentration of antimony was much lower at control sites, it was in a more labile form; none of the antimony was in the residual fraction. Little is known about the adsorption of antimony to soil. Limited studies indicate that antimony may be fairly mobile under diverse environmental conditions (Rai and Zachara 1984). Since antimony forms anionic species, adsorption should be greatest under weakly acidic conditions. Antimony's adsorption to soil and sediment is primarily correlated with the iron, manganese, and aluminum content; it coprecipitates with hydroxylated oxides of these elements.

As a natural constituent of soil, antimony is transported into streams and waterways from natural weathering of soil as well as from anthropogenic sources. Antimony has a low occurrence in ambient waters. In a survey of dissolved antimony in ambient waters performed by the U.S. Geological Survey, only 6% of 1,077 survey measurements were above the probable detection limit of 5 ppb (Eckel and Jacobs 1989). Antimony concentrations in groundwater appear to be similar to that in surface water. Mean antimony concentrations in surface and groundwater at hazardous waste sites were 27 and 35 ppb, respectively (CLPSD 1989). The forms of antimony and the chemical and biochemical process that occur in the aquatic environment are not well understood. Antimony in both aerobic freshwater and seawater is largely in the +5 oxidation state, although antimony in the +3 oxidation state also occurs in these waters. Trivalent antimony is the dominant oxidation state of antimony in anaerobic water. Antimony can be reduced and methylated by microorganisms in anaerobic sediment, releasing volatile methylated antimony compounds into the water. Methylstibonic acid and dimethylstibonic acid occur in natural water; the monomethyl species is the more abundant one (Andreae 1983; Andreae and Froelich 1984).

EPA has identified 1,177 NPL sites. Antimony and its compounds have been found at 52 of the sites evaluated for the presence of these chemicals (View 1989). However, we do not know how many of the 1,177 NPL sites have been evaluated for these chemicals. As more sites are evaluated by EPA, the number may change. The maximum concentrations of antimony reported at these sites are 2,100 ppb in groundwater, 1,000 ppb in surface water, and 2,550 ppm in soil. The frequency of these sites within the United States can be seen in Figure 5-1.

The general population is exposed to low levels of antimony in ambient air and food. The average intake of antimony from food and water is roughly

FIGURE 5-1. FREQUENCY OF NPL SITES WITH ANTIMONY CONTAMINATION *

FREQUENCY   ⊞⊞⊞ 1 SITE   ⊞⊞⊞ 2 TO 3 SITES

▦▦▦ 6 SITES   ■■■ 14 SITES

* Derived from View 1989

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5 µg/day (Iyengar et al. 1987). The intake from breathing air is generally a small fraction of that from ingestion. Exposure from antimony trioxide, which is used extensively in textiles and plastics as a fire retardant, is not expected to be significant. EPA estimates that approximately 4,000 workers may be exposed to antimony and antimony trioxide in production facilities and first-level processing facilities. These workers will have the highest levels of exposure to antimony. The highest air concentration of antimony reported in workplace surveys was 6.2 mg/m^3.

5.2 RELEASES TO THE ENVIRONMENT

Most analytical methods for antimony in environmental samples do not distinguish between antimony metal, antimony trioxide, or other compounds of antimony. More sophisticated methods are required to determine the oxidation state of antimony or the nature of its binding to soil and particulate matter; therefore, it is generally impossible to say with certainty what forms of antimony are released from natural and anthropogenic sources, what forms are deposited or occur in environmental samples, and to what form of antimony people are exposed. The form of antimony will have significant consequences as far as its transport, transformations, and bioavailability are concerned.

5.2.1 Air

Antimony and its compounds are natural components of the earth's crust and releases to the atmosphere result from natural as well as anthropogenic sources. A recent assessment of natural sources of atmospheric trace metals paid special attention to biologic origins of these metals. Nriagu (1989) estimated that 41% of antimony emissions to the air are from natural sources. The natural sources and their median percentage contribution are: wind-borne soil particles, 32.5%; volcanoes, 29.6%; sea salt spray, 23.3%; forest fires, 9.2%; and biogenic sources, 12.1%. Previous assessments indicated that natural inputs were minor compared with anthropogenic ones; in one estimate, anthropogenic sources contributed 39 times more antimony than did natural sources (Lantzy and Mackenzie 1979; Yocom 1983).

Anthropogenic sources of antimony releases to the atmosphere include nonferrous metal mining, nonferrous metal primary and secondary smelting and refining (Crecelius et al. 1974; Pacyna et al. 1984), coal combustion (Gladney and Gordon 1978), and refuse and sludge combustion (Greenberg et al. 1978). Table 5-1 lists the air releases by state from facilities that produce, process, and use antimony and its compounds according to the 1987 TRI (1989). Releases to air total 135,627 pounds. The highest annual release reported by a single company is 29,900 pounds. The industries that contribute the bulk of releases are those that produce antimony and antimony trioxide. Since the TRI does not include emissions from power plants and refuse and sludge incinerators, their estimate of antimony emissions is not complete. European emissions of antimony were estimated at 380 tons for 1979 (Pacyna et al. 1984). Volatile elements and chalcophilic elements (those elements showing an

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association with sulfur), like antimony, show large enrichment over crustal abundances in particulate matter emitted from smelting, coal combustion, and refuse combustion. The ranges of enrichment factors reported for these sources are 10,300-l,000,000, 20-140, and 3,000-10,000, respectively (Gladney et al. 1978; Gordon and Sheffield 1986; Small et al. 1981). On a global basis, metal smelting is estimated to make more than double the contribution to atmospheric emissions as other sources, but long-term coal combustion is anticipated to be a dominant factor in future tropospheric antimony levels (Austin and Millward 1988). The antimony that is associated with fine particles (less than 1 pm) tends to result from combustion and other high temperature sources, while that associated with large particles (greater than 10 pm) is likely to originate from wind-blown soil and dust (Schroeder et al. 1987).

It is estimated that 3 g of antimony are released from copper smelters for each ton of copper produced (Pacyna 1984). Typical concentrations of antimony observed in plumes of five copper smelters ranged from 58 to 370 ng/m^3 versus an average background level of 2 ng/m^3 in ambient air (Small et al. 1981). It was found that most of the antimony deposited close to one smelter originated from ground-level emissions (e.g., fugitive emissions) rather than stack emissions (Ainsworth 1988). It was determined that between 57% and 66% of the antimony in the stack of a plant that recycled lead storage batteries was in the vapor form (Craig et al. 1981). This antimony will recondense onto small particles.

The antimony content of 166 American coal samples ranged from 0.1 to 8.9 ppm, with a mean content of 1.15 ppm (Sabbioni et al. 1983). Therefore, it would be expected that coal-fired power plants are a significant source of antimony emissions. A typical, modem coal-fired power plant emits about 31 µg of antimony per kilogram of fuel burned, compared with 3.9 µg/kg for an oil-fired plant (Hasanen et al. 1986). Heavy fuel oil has an antimony content of about 0.067 ppm. Emissions from two units of the Columbia Station coal-burning power plant in Portage, Wisconsin, ranged from 220 to 1,300 ng antimony/m^3 when sampled over 1.5 years (Bauer and Andren 1988). Another investigator reported that a coal-fired power plant with pollution control had stack emissions of 6,800 ng antimony/m^3 (Lee et al. 1975). Antimony in these emissions tends to be associated with fine particles and the surface of particulate matter, consistent with their formation by volatilization and subsequent condensation (Hansen and Fisher 1980). In a modern coal plant, 69% of antimony emissions were associated with particles less than 3 µm in diameter (Sabbioni et al. 1984). Two other studies found that 34-52% of emissions from coal-fired power plants were associated with particles less than 2 µm, and that the mass medium diameter (MMD) of particles from a plant with pollution control devices was 0.6 µm (Gladney et al. 1978; Lee et al. 1975).

A study of emissions from two municipal incinerators in Washington, D.C., showed that refuse incineration can account for the major

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portion of antimony in urban aerosols (Greenburg et al. 1978). At least 90% of this antimony is associated with respirable, fine particles that are less than or equal to 2 μm in diameter. The concentration range of antimony in suspended particles from these incinerators was 610-12,600 ppm, with a mean concentration of 2,400 ppm. In performance tests conducted under the Canadian National Incinerator Testing and Evaluation Program, 2.3 g antimony/ton of refuse was emitted under normal operating conditions. Under a range of operating conditions, the amounts ranged from 1.9 to 9.6 g antimony/ton (Hay et al. 1986). Respective stack antimony concentrations were 0.6 and 0.5-2.6 mg/Nm^3 at 12% CO_2, where Nm3 indicates standard cubic meter (1 atmosphere, 25°C). A European study gave emission factors for refuse and sewage sludge incinerators as 4.55 and 1.9 g antimony/ton, respectively (Pacyna 1984). All of the antimony from the stack of a refuse-burning plant was in particulate rather than gaseous form (Braun et al. 1983).

Antimony is a component of ammunition, and therefore antimony may be emitted during the discharge of firearms. This source of emission is inconsequential outdoors. However, in indoor firing ranges, it is a significant source of antimony emission (Dams et al. 1988; Olmez et al. 1985).

An air monitoring study was conducted in 1982 at three sites surrounding the Anaconda Minerals Company smelter facility in Montana. This company had closed 2 years earlier after 8 decades of operation. The study was performed under Superfund to ascertain whether the accumulated heavy metals released during the smelting operations and from tailing ponds might become reentrained by wind and pose a health hazard (Ives et al. 1984). While no antimony was reported to have been produced at the Anaconda Minerals Company facility, many of the metals that were extracted, (e.g., copper, lead, arsenic) are found in association with antimony. The atmospheric levels of heavy metals were very low, indicating that there was not any significant reentrainment of heavy metals from tailing ponds or smelter deposits. The particulate matter examined was generally crustal or carbonaceous in character. Antimony was detected on only 3 of 85 air sampling filters at the three sites.

Stibine may be produced in lead acid battery plants during the formation process. During this process, an electric current is passed through the battery plates, reducing PbO to Pb at the negative plate, and oxidizing PbO to PbO_2 at the positive plate. Hydrogen gas is released that can react with the antimony in the grid metal to form stibine (Jones and Gamble 1984). Stibine may also be formed during remelting of mixed lead-calcium and lead-antimony battery scrap, the former being used for starter batteries. In this process, the intermetallic compound calcium antimonide may be produced in the dross or scum. This compound releases stibine when it comes in contact with water (Ayhan et al. 1982).

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5.2.2 Water

Antimony is a natural constituent of soil and is transported into streams and waterways in runoff either due to natural weathering or disturbed soil. Much of this antimony is associated with particulate matter. In the EPA-sponsored National Urban Runoff Program in which 86 samples of runoff from 19 cities throughout the United States were analyzed, antimony was found in 14% of runoff samples at concentrations ranging from 2.6 to 23 ppb (Cole et al. 1984).

Estimated releases of antimony to water from facilities in the United States that produced, processed, and used antimony in 1987 according to the TRI are found in Table 5-1. These releases totaling 62,328 pounds are much lower than those to air or land. A survey of raw and treated waste water from 20 industrial categories indicates that antimony is commonly found in some waste waters. Those industries with mean effluent levels exceeding 1 ppm in raw waste water were (industry [mean level in ppm]): foundries (1.1), porcelain enameling (1.4), and nonferrous metal manufacturing (5.7) (EPA 1981). The maximum levels in discharges from these industries were 3.4, 22, and 80 ppm, respectively. Additionally, four other industrial categories had maximum concentrations exceeding 1 ppm. These were laundries (2.4 ppm), inorganic chemical manufacturing (1.4 ppm), ore mining and dressing (3.8 ppm), and paint and ink formulation (2.2 ppm). For treated waste water, only porcelain enameling had mean antimony levels in excess of 1 ppm. The levels reached 4.3 ppm.

Domestic waste water is a potential source of antimony in waterways. Concentrations of antimony in influents to 11 municipal waste water treatment plants (POTWs) (155 observations) ranged from 0.0003 to 2.1 ppm; the median value was approximately 0.1 ppm (Minear et al. 1981). Antimony is not well removed in POTWs, and releases from these facilities may contribute to releases of antimony to water (Aulenbach et al. 1987; EPA 1981). The outfall of a sewage treatment plant in Seattle, however, did not appear to make a significant contribution to the antimony levels in the sediment of Puget Sound (Crecelius et al. 1975).

Waste water generated from mining and smelting operations comes from seepage, runoff from tailing piles, or utility water used for mine operation. In addition to liquid effluent from smelting operations, slag may be dumped directly into receiving waters (Crecelius et al. 1975). These discharges largely contain insoluble silicates and sulfides which readily settle out. Total antimony in effluent from a primary aluminum production facility was 40 ppb (Rawlings 1980). Sixty percent of this antimony was subsequently removed by lime coagulation.

One of the potentially dangerous sources of chemical release at waste sites is from leachate. Leachate from three municipal landfills in New Brunswick, Canada, each contained 0.01 ppm of antimony (Cyr et al. 1987).

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The antimony concentration in sediment at two sites below the leachate outfalls was 23.9 ppm (dry weight) and nondetectable, respectively.

5.2.3 Soil

Most of the antimony released to the environment is released to land. According to Table 5-1, which shows the estimated releases in 1987 of domestic industries that produce, process, or use antimony, 2,845,131 pounds of antimony are released to land, constituting 93% of environmental releases reported to TRI (TRI 1989). The industries that release the largest amount of antimony are the smelters that produce antimony and antimony trioxide. Much of this release is slag, which is the residue from smelting operations. Other releases to land include sludge from POTWs and municipal refuse.

An analysis of the concentration of antimony at hazardous waste sites at the Contract Laboratory Program Statistical Database (CLPSD) shows that antimony was reported in 153 of 1,307 soil samples, with geometric mean and maximum levels in positive samples of 8.0 and 330 ppm, respectively (Eckel and Langley 1988). An analysis of these data indicates that 7.3% of the CLPSD samples exceed the number expected to be above the 95% upper confidence limit for background U.S. soils (Eckel and Langley 1988). The CLPSD includes both NPL and non-NPL data. A more recent update of the CLPSD reports a 12.8% occurrence of antimony and a geometric mean concentration of 16.86 ppm (CLPSD 1989). No analysis was performed on these results to indicate what percentage exceed the background levels of antimony normally found in soil.

5.3 ENVIRONMENTAL FATE

It is not always possible to separate the environmental fate processes relating to transport and partitioning from those relating to transformation for a metal and its various compounds and complexes. Part of this problem is that the form of a metal is rarely identified. A change of mobility may result from a transformation of a metal to a more or less soluble form. Adsorption may be the result of the formation of strong bonds (transformation) as well as weak bonds. Information regarding the deposition and general adsorption of antimony is in Section 5.3.1 and information regarding the areas of environmental fate where speciation is discussed is in Section 5.3.2.

5.3.1 Transport and Partitioning

Antimony is released to the atmosphere in the form of particulate matter or adsorbed to particulate matter. It is dispersed by wind and removed by gravitational settling and dry and wet deposition (Schroeder et al. 1987). The removal rate and distance traveled from the source will depend on source characteristics (e.g., stack height), particle size and density, and meteorological conditions.

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Gravitational settling governs the removal of large particles (greater than 5 μm), whereas smaller particles are removed by the other forms of dry and wet deposition. Removal of coarse particles may occur in a matter of hours. Very small particles may have an atmospheric half-life as long as 30 days (Schroeder et al. 1987). Antimony is predominantly associated with small, submicron particles (Stoessel and Michaelis 1986). This is frequently the case with the more volatile metals, such as antimony, that may volatilize during combustion and condense when cooled. A model which relates particle size to volatility estimates an average atmospheric half-life for antimony of 1.9 days; for the more volatile antimony trioxide (see Table 3-2), the estimated half-life is 3.2 days (Mueller 1985). With such an atmospheric half-life, antimony may be transported far from its source. Evidence of this was reported by Animoto and Duce (1987), who stated that the antimony levels in aerosols at the Enewatak Atoll in the tropical North Pacific were higher than those expected from seawater or crustal material.

Metal deposition is characterized by large temporal and spatial variability. Estimated antimony deposition rates in urban areas are 0.006 and 0.004 kg/hectare/year (60 and 40 ng/cm^2/year) for dry and wet deposition, respectively (Schroeder et al. 1987). For remote areas, bulk (wet plus dry) deposition may be as little as 0.00016 kg/hectare/year (1.6 ng/cm^2/year). Rates of air-sea transfer of antimony are similar to the rates of accumulation of antimony in sediment (Arimoto and Duce 1987).

The partitioning between dry and wet deposition depends on the intensity and duration of precipitation, the element in question, its form in the particulate matter, and its particle size. The ratio of wet to dry deposition generally increases with decreasing particle size; therefore, a larger proportion of antimony will be found in rain compared with most other metals. A study of the wet and dry deposition over an 8-week period on an island in the German Bight, which was presumably far from sources, found 87% of deposited antimony dissolved in rain, 11% in particulate matter in rain, and only 2% as dry deposition (Stoessel and Michaelis 1986). In other studies conducted in areas removed from sources of antimony emissions, half of the antimony deposition was in the form of wet deposition (Ainsworth 1988). The total antimony deposition annualized from a B-month study in an industrial area of England where a number of ferrous and nonferrous metal smelting and manufacturing works were concentrated was 1,000 ng/cm^2-year (a factor of 20-40 above nonurban deposition rates) (Pattenden et al. 1982). Of this, 42% represented wet deposition, of which 58% was dissolved antimony.

Antimony released into waterways is generally associated with particulate matter; it is transported to and settles out in areas of active sedimentation such as where a river empties into a lake or bay (Beijer and Jernolov 1986). Similarities in the composition of suspended river sediment and the sediment in bays indicate that the rivers transport the suspended sediment and deposit it in the bottom sediment (Crecelius et al. 1975). Additionally, when a river feeds into an estuary, the salinity changes that

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are encountered may affect adsorption to sediment and particulate matter, complexation, and coprecipitation.

Little is known of the adsorptive behavior of antimony, its compounds, and ions. The binding of antimony to soil is determined by the nature of the soil and the form of antimony deposited on the soil. Some forms of antimony may bind to inorganic and organic ligands. On the other hand, a mineral form would be unavailable for binding. Some studies suggest that antimony is fairly mobile under diverse environmental conditions (Rai and Zachara 1984), while others suggest that it is strongly adsorbed to soil (Ainsworth 1988; Foster 1989; King 1988). Since antimony has an anionic character (e.g., Sb(OH)i), it is expected to have little affinity for organic carbon. No information could be found about antimony's adsorption to clay minerals. It is not expected that cation exchange, which generally dominates adsorption to clay, would be important for anionic antimony. Antimony is known to form coprecipitates with hydrous iron, manganese, and aluminum oxides in soil and sediment (Callahan et al. 1978).

The capacity of soil to adsorb antimony and the nature of the bound antimony were evaluated by incubating 200 ppm of antimony potassium tartrate with 5 g samples of soils for 6 days (King 1988). Thirteen soils and subsoils (21 samples) from the southeastern United States (10 mineral and 3 organic) were included in the study. Antimony adsorbed strongly to most soils. The amount of adsorbed antimony ranged from 50% in Lakeland surface soil to 100% in several soils; the median percent adsorption was 93%. The percentage of nonexchangeable (i.e., that not removed with KCl) antimony adsorbed paralleled that of total antimony and ranged from 57% to 99%. Both sorbed and nonexchangeable antimony were negatively correlated to sand content in mineral soil. The soil/water partition coefficient (mmol/kg soil)/(mol/m^3) was 81 and greater than 185 for organic and mineral soils, respectively. Several mineral soils adsorbed 100% of the antimony and were excluded from the averaging. It is not clear what species of antimony was adsorbed in this study. If it was the antimony tartrate ion, the study may not be particularly relevant to other forms of antimony. The mobility of antimony in clay, sandy loam, silt loam, and sand soils was investigated using soil thin-layer chromatography (TLC) (Foster 1989). The antimony was applied as antimony trioxide in a water or 1% HCl suspension and developed with water in 8 hours or less. Despite experimental difficulties, the results demonstrated that there is no general mobility of antimony in any soil. The experimental problems and the fact that small amounts of antimony were found in all zones is possibly due to an unsuitable soil digestion (Ainsworth 1988).

A Superfund site study at a battery reclamation plant showed that while soil and sediment contained high levels of antimony, an aquifer 3 m below the surface contained 0.1 ppm of antimony; no antimony was detected in two deeper aquifers (Trnovsky et al. 1988). Antimony adsorbs strongly to colloidal material in soil. The partition coefficient of antimony to 0.05-0.003 μm

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colloids was 1,300. Antimony adsorbed to such material can be transported with the colloids in groundwater (Buddenmeier and Hunt 1988).

Leaching experiments performed with river sediment samples from a mintng district in Idaho indicated that Sb(V) was the major species released during leaching (Mok and Wai 1990). The fraction of antimony leached from sediment with deionized water after 10 days was highly correlated with the free iron and manganese oxide content of the sediment (correlation coefficients of 0.90 and 0.75). Experiments were also performed in which the pH dependence of leaching was determined. The release of antimony from the sediment increased at low pH and increased sharply at high pH. The form of released antimony was also sensitive to pH. At pH 2.7, the bulk of antimony released was as Sb(II1); at pH 4.3, the concentrations of tri- and pentavalent antimony were comparable; and at pH 6.3 and above, Sb(V) was the predominant species.

In order to evaluate the potential for leaching of elements from landspread sewage sludge, Gerritse et al. (1982) studied the adsorption of elements from water, salt solutions, and sludge solutions to sandy and sandy loam top soils. They used metal levels that occur in the solution phase of sewage sludge, lo-100 ppb in the case of antimony. The results indicate that antimony is fairly mobile in these soils. The adsorption constants were approximately 2-16 in the sandy soil and 20 in the sandy loam soil. Although the presence of sludge increases the mobility of many trace elements because of complexation with dissolved organic compounds or increased ionic strength, this did not appear to be the case with antimony (Gerritse et al. 1982). It is not easy to reconcile these results with those of Foster (1989), Ainsworth (1988), Trnovsky et al. (1988), or Van der Sloot et al. (1982). These studies indicated that antimony deposited on the soil surface accumulates primarily in the surface layer, and that aquifers beneath antimony waste piles are not grossly contaminated.

Mobilization of elements deposited on soil in fly ash is a potential source of terrestrial and aquatic pollution. When the alkaline fly ash from a coal-fired power plant was packed in a column and subject to leaching with dilute sulfuric acid, antimony was partially dissolved and removed from the upper layers of ash and deposited and retained on lower sections of ash in the column (Warren and Dudas 1988). It was thought that extractable, surfaceadsorbed antimony in the upper layers of ash was removed by the acid, subsequently precipitated by iron oxyhydroxides, and retained lower down in the column. Other column leaching and shake-flask experiments with coal ash are too complex to summarize; they basically indicate that leaching of antimony is low. Low concentrations of antimony found in groundwater beneath precipitator ash ponds lend field confirmation to the laboratory results (Van der Sloot et al. 1982).

When saline sediment is oxidized, such as when dredged sediment is exposed to oxygen, the pH can become very low (pH 3.1 in a lab experiment), and antimony and other toxic metals may be released (DeLaune and Smith 1985).

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This occurs because sediments in estuaries often contain pyrite and other readily oxidizable sulfur compounds; sulfuric acid may be produced and overwhelm the buffering capacity of the sediment. An analogous pH decrease following oxidation was not observed in a freshwater sediment.

Antimony does not appear to bioconcentrate appreciably in fish and aquatic organisms. No detectable bioconcentration occurred during a 28-day test in bluegills (EPA 1980). Only low levels of antimony have been reported in fish and aquatic organisms collected off the coast of Africa, Australia, and the Danube River in Austria (Callahan et al. 1978; Maher 1986). Bioconcentration factors for antimony ranged from 0.15 to 390 (Acquire 1989; Callahan 1978). A study of the distribution of antimony around a smelter site indicated that antimony occurring in plants results from surface deposition. Uptake from soil is minor and appears to be correlated with the amount of available antimony (that which is soluble or easily exchangeable) (Ainsworth 1988). Antimony bioconcentration was measured in voles, shrews, rabbits, and invertebrates around a smelter. Analysis of antimony in organs of the small mammals, compared with estimates of their antimony intake from food, showed that, although the amount of antimony in the organs was elevated, it was low compared to the amount ingested. The results suggest that antimony does not biomagnify from lower to higher trophic levels in the food chain.

5.3.2   Transformation and Degradation

5.3.2.1   Air

Little is known about the chemical forms and physical and chemical transformations of trace elements in the atmosphere. This is primarily because analytical methods provide information concerning the metal content rather than the specific compounds or species. Studies at an antimony smelter suggest that emissions consist of antimony oxide (Ainsworth 1988). In the absence of specific information, it is generally assumed that elements of anthropogenic origin, especially those emanating from combustion sources, are present as the oxide. Windblown dust particles may contain antimony in mineral species, such as sulfides and oxides, and are associated with silicates.

When released into the atmosphere as an aerosol, antimony is believed to be oxidized to antimony trioxide by reaction with atmospheric oxidants. Antimony trioxide particles do not undergo changes in chemical composition, particle size, or morphology after emission; however, a surface coating of sulfate may form (Ainsworth 1988).

5.3.2.2   Water

There is relatively little information available regarding the behavior of antimony in the aquatic environment. Since the dissolved state is the phase in which transfers to suspended matter, organisms, and sediment occur,

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it is especially important to know the oxidation state and forms of the antimony that is dissolved. This is particularly difficult for antimony because the levels of total antimony in water are so low. Thermodynamically, most dissolved antimony in natural waters under aerobic conditions should be present in the +5 oxidation state as antimonate species. At 0.001 M total antimony, the dominant species were $Sb(OH)_6^-$ and $Sb(OH)_5^0$ (Rai et al. 1984). A small quantity of polymeric hydroxy species were found, but these will be less significant when the total antimony concentration is low, such as in natural water. While industrial inputs will commonly contain antimony in the +3 oxidation state (e.g., antimony trioxide), it is not known how fast antimonite would oxidize to antimonate under natural conditions. Under reducing conditions, trivalent species such as $Sb(OH)_3^0$, $Sb(OH)_4^-$, and $Sb_2S_4^{4-}$ may be significant (Andreae and Froelich 1984; Rai et al. 1984).

Antimony compounds may undergo photochemical reactions, but these do not appear to be significant in determining their aquatic fate (Callahan et al. 1978). Antimony trioxide suspensions strongly absorb ultraviolet radiation below 325 nm and darken. The process is reversible, and when the light is removed, the white color slowly returns (Markham et al. 1958). The effect is believed to be due to peroxide radical formation on the crystal surface. Both water and oxygen seem to be necessary for the reoxidation of the reduced antimony.

Antimony can be reduced and methylated by microorganisms in the aquatic environment, similar to arsenic, and become mobilized (Andreae et al. 1983; Austin and Millward 1988). This reaction is most likely to occur in reducing environments, such as in bed sediment. In the case of arsenic, this reaction may be mediated by fungi and bacteria (Beijer and Jernelov 1986), but it is not known whether this is the case with antimony. The resulting trimethylstibine is initially oxidized by atmospheric oxygen to a mixture of trimethylstilbine oxide ($(CH_3)_3SbOH$) and trimethylstibinic acid ($(CH_3)_2SbO_3H$), and then to antimony oxides and insoluble polymers (Parris and Brinckman 1976). The rate constant is estimated to be of the order of 0.1 to 0.2 L/mol-sec. Trimethylstibine has a high vapor pressure, 103 mmHg at 25°C, and might volatilize before it is completely oxidized. The oxidation product, $(CH_3)_3SbO$, is much more soluble than trimethylstibine; therefore, oxidation will reduce volatilization (Callahan et al. 1978). Oxidation of trimethylstibine in the gas phase is very rapid; the rate is 0.11/mmHg-sec or 2000 L/mol-sec. Trimethylstibine has been shown to react with alkyl iodides and bromides; this results in the formation of quaternary salts (Parris and Brinckman 1975). Should antimony occur in a landfill with alkyl halides, the formation of quaternary salts should greatly enhance antimony's mobility.

The chemical and biochemical transformations of antimony in natural waters are not well understood. There are only a few studies that describe the antimony species present in various systems and their transformations. A study of the waters of the Ochlockonee River estuary revealed the presence of Sb(III), Sb(V), methylstibonic acid, and dimethylstibonic acid (Andreae 1983).

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The concentration of all four species increased with the salinity of the water. For freshwater, the concentrations were about 18, 3.3, and 1 ng antimony/L (ppt) for Sb(V), Sb(III), and methylstibonic acid, respectively; dimethylstibonic acid was not detectable. The concentration of Sb(V) and Sb(II1) increased linearly with salinity, reaching 135 and 11 ppt, respectively, in the ocean. An analogous increase in the level of the methylated forms with salinity was nonlinear, suggesting that these forms are consumed in the estuary. In seawater, levels of methylstibonic acid and dimethylstibonic acid were 12.5 and 1.5 ng antimony/L (ppt), respectively. It was reported that the Sb(III) levels were approximately 2% that of Sb(V) in samples of sea water and river water (Mok and Wai 1987). In a sample of river water from the Kellogg mining district in Idaho, the contribution of Sb(III) was only 0.4% (0.03 ppb compared with 7.03 ppb of Sb(V)). More recent studies in Idaho indicated that 1-4% of antimony was in the trivalent form in a river receiving mining leachate, while at a site on an unpolluted fork of the same river, the fraction was 17% (Mok and Wai 1990).

The depth profile of antimony species in the Baltic sea showed that Sb(V) was the most abundant species in the oxic zone, although Sb(III) was detectable throughout the water column (Andreae and Froelich 1984). A maximum for Sb(III) in the oxic zone was sometimes noted in the surface layer and is believed to result from biological activity. There is evidence that phytoplankton can reduce Sb(V) to the Sb(III). Sb(III) decreases to very low levels at the base of the seasonal thermocline and remains low down to the sediment where increasing levels are again observed. Sb(III) only accounts for 44% of the inorganic antimony in the anoxic zone, and speciation in this region is unclear. Thermodynamically, the antimony should be in the trivalent state. Thiocomplexes are thought to account for some of the antimony in this zone. Methylated antimony species existed throughout the water column and made up 10% of total antimony. Monomethyl antimony species were more abundant in surface waters and in the anoxic zone. There was no sharp increase in methyl antimony near the sediment, which would be expected if these species were formed biosynthetically. Since the highest antimony concentration is at the surface, it is unlikely that antimony is taken up by phytoplankton, as is the case with arsenic. A decrease in antimony concentration with depth suggests scavenging by particulate matter and, at lower depths, by iron hydroxyoxides.

Sea water samples off the Belgian coast were analyzed using oxidation, UV irradiation, and anodic stripping voltammetry to distinguish bound antimony and to identify its oxidation state (Gillian and Brihaye 1985). The concentration of total antimony ranged from 0.05 to 0.38 ppb. The study showed that antimony was mainly present as Sb(V), and the percentage complexed to organic matter varied between 20% and 60%. This results is surprising because antimony occurs as anionic species in water and these are not expected to complex with organic matter. These results have not been confirmed by other investigators. The concentration of Sb(II1) was below the detection limit (0.005 ppb) at almost all sites. The exception was the coastal sites

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where it ranged up to 0.039 ppb. Antimony found in rain and snow is predominantly in the +5 oxidation state (Metzger and Braun 1986).

Information concerning the behavior of antimony in sediment is extremely limited. Investigators would like to know how strongly antimony is bound in sediment and what the potential is for long-term mobilization. A study was conducted of sediments in Puget Sound, Washington, where a copper smelter discharges large amounts of antimony (Crecelius et al. 1975). In 23 noncontaminated sediment samples, antimony concentrations correlated with organic carbon and fine-grained particles; however, since these sediments are also associated with hydrous-iron oxides, further investigations on the association of antimony in sediment were conducted and showed that less than 10% of the antimony in both contaminated and uncontaminated sediment was bound to readily oxidizable organic matter. Extraction with oxalate and citratedithionite-bicarbonate suggested that roughly half of the antimony in uncontaminated sediment and less than 20% of that in contaminated sediment was bound to extractable iron or aluminum compounds. Most of the antimony in the polluted water was bound to chemically stable slag.

Experiments were performed in which the forms of antimony in sediment were evaluated after the sediment was incubated under anaerobic conditions for 45 days (Brannon and Patrick 1985). Ten dredged, contaminated sediments that were obtained from various locations in the United States were used as is or amended with 75 ppm antimony potassium tartrate. An extraction procedure was used that identified the antimony in interstitial water and in "exchangeable," "easily reducible," and "moderately reducible" sediment fractions. Essentially all antimony in the unamended sediment was in a "moderately reducible" phase (oxalate extraction). The same was generally true for 7 of the 10 sediments that were amended with potassium antimony tartrate. In the other three sediments, the greatest proportion of antimony was in the "easily reducible" fraction. A small fraction of the antimony-amended sediment (but none of the unamended sediment) was contained in the more potentially mobile interstitial water and "exchangeable" fraction. It should be stressed that since the amended samples had higher antimony levels, small percentages in different fractions were more readily detectable than for the unazíended sediment. The high correlation of antimony with the "moderately reducible" fraction indicates that hydrous iron and aluminum oxides were affecting the fixation of antimony. These hydrous oxides are positively charged under environmental conditions and bind the anionic antimony. The samples were subjected to 6 months of aerobic leaching. Unamended samples released antimony very slowly, compared with amended samples, indicating the higher amounts of mobile antimony in the latter samples. Antimony-amended sediments lost from 3.6% to 32% of their antimony during leaching; unamended sediments lost from 0% to 23% of their antimony. The sediment/water distribution coefficient ranged from 3.3 to 27.5 in amended sediments, compared with values up to 1,183 in unamended sediments. The distribution coefficient correlated with iron in both amended and unamended sediment; additionally, it correlated with calcium carbonate in amended sediment. After aerobic leaching, there was

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an increase in antimony in the "moderately reducible" phase and a decrease in the "easily reducible" phase that paralleled changes in iron concentrations. Volatile antimony compounds were formed in seven of the amended sediments but in none of the unamended sediments; they escaped through the overlying water independently of the redox state of the water (i.e., aerobic or anaerobic).

When 10 and 100 ppm antimony trioxide with added nutrients was incubated with natural bottom sediment from Puget Sound under aerobic or anaerobic conditions for up to 120 days, three organoantimony biotransformation products were found in solution after 60 days (Martinson 1988). Two of these were identified as methylstibonic acid and dimethylstibonic acid. No determination of rate or conditions affecting the transformation was made. However, it was estimated that much less than 0.1% of the antimony present was transformed.

Few data are available on the removal of antimony in the activated sludge process used in water treatment plants. In one laboratory simulation, mixture of metals at levels considered typical of industrial/domestic sewage (0.1 ppm antimony) was continuously added to the influent of the treatment system. No antimony removal was observed (Kempton et al. 1983).

5.3.2.3   Soil

Little is known about the behavior of antimony on soil during weathering. In aerobic surface soils, oxidation generally occurs. Antimony trisulfide in ore deposits is known to be oxidized by soil bacteria (Ainsworth 1988). Methylated antimony compounds, similar to those formed in sediment, may be formed in waterlogged soil.

The form and availability of antimony in soil is determined by measuring antimony's extractability with different solvents. A sequential extraction procedure was used to determine the form of antimony in soil around a stibnite smelter and to compare it with that found at a control site (Ainsworth 1988). The extraction procedure used could identify the following fractions of antimony: soluble or bound to ion-exchange sites and, therefore, available; bound to carbonates; bound to manganese oxides that are easily reduced; bound to iron oxides that are less easily reduced; bound to organic matter; and residual antimony that was not incorporated into silicates (Ainsworth 1988). Results of the study showed that the distribution pattern among the various fractions was different at the smelter and control sites. Three quarters of the total extracted antimony in surface (0-5 cm) soil near the smelter was in the residual fraction; none of the antimony in the control site was in this fraction. The remainder of antimony in soil from the smelter site was more or less equally distributed among the other fractions. Higher proportions of the antimony at the control site were in the readily available fraction, bound to manganese oxides, or complexed with organic matter, compared to the smelter site. Because of the low concentration of antimony in the control-site soil, fractional determinations are less accurate than for sites near the smelter. For subsoil (greater than 15 cm depth) from the smelter site, less antimony

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was found in the residual fraction (62%), and more antimony was in the available fraction, bound to carbonates, or bound to iron oxides than in the surface sample. The factors determining the distribution of antimony between fractions is unclear. The absence of any residual fraction at the control site has been explained by assuming that antimony-containing mineral has been completely broken down.

Near the smelter, antimony deposits have a different character than further away since they are derived from fugitive emissions rather than stack deposition. In a 3-month study of deposition of antimony from the smelter, about one-third to one-half of the deposited antimony at the smelter site was soluble, compared with about one-half to two-thirds at other sites. Since antimony in rain near the smelter site was soluble, it appears that once deposited on soil, antimony rapidly converts to more insoluble forms.

5.4   LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1   Air

There are insufficient data regarding antimony concentrations in the atmosphere for representative general mean or median concentrations to be reported. Antimony concentrations in air particulate matter in remote, rural, and U.S. urban areas are 0.00045-1.19, 0.6-7, and 0.5-171 ng/m^3, respectively (Austin and Millward 1988; Schroeder et al. 1987). No vapor-phase antimony has been reported. Antimony concentrations over the North Atlantic and North Pacific are 0.086 and 0.0037 ng/m^3, respectively (Arimoto and Duce 1987; Austin and Millward 1988). Two values reported for antimony in aerosols in clean continental and marine environments are 0.2 ng/m^3 at the Jungfraujoch in the Swiss Alps and 0.00045 ng/m^3 at American Samoa (Austin and Millward 1988). The mass median aerodynamic diameter of antimony-containing aerosols from a range of areas remote from anthropogenic sources was 0.86 μm (Milford and Davidson 1985). The mass size distribution is bimodal, with the larger peak at about 0.6 μm and a smaller one at about 3 μm. An example of the size distribution of antimony-containing particles removed from anthropogenic sources was obtained in an 8-week study on an island in the German Bight. The concentration of antimony in a size fraction increased as the size decreased. The antimony concentration ranged from 0.03 ng/m^3 for particles greater than 7.2 μm to 0.3 ng/m^3 for particles less than 0.5 μm (Stoessel and Michaelis 1986).

Several studies show that antimony can travel long distances, and that ambient levels may reflect the origin of the air masses. The geometric mean antimony concentration in aerosols at three rural/remote locations in New York state was 1.0, 0.72, and 0.33 ng/m^3 (Dutkiewicz et al. 1987), and the enrichment over crustal abundance ranged from 920 to 1,650. The enrichment factor is smaller but similar to the mean enrichment factor of 1,880 for antimony in 29 cities (Gladney et al. 1984). The high enrichment indicates that the antimony is of anthropogenic origin. An analysis of the New York

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State data using backward-in-time air trajectories is consistent for the Midwest being the dominant source of antimony. An analysis of European sources and wind trajectories further illustrate that antimony may be transmitted over long distances. The average concentration at a city in southern Norway was 0.54 ng/m^3 when the air masses came from the United Kingdom, and 0.07 ng/m^3 when they came from over the Atlantic (Hillamo et al. 1988).

Twenty-four-hour samples collected at 10 locations in Washington, D.C., yielded average antimony concentrations ranging from 1.1 to 3.0 ng/m^3 (Kowalczyk et al. 1982). As a result of a chemical element balance analysis, the three major contributing sources in order of decreasing significance are believed to be refuse incineration, motor vehicles, and coal combustion. In a Houston study, the range of antimony concentrations in fine (0.1-2.5 μm) aerosols was 0-12 ng/m^3, whereas that in particles greater than 2.5 μm was 0-4 ng/m^3 (Johnson et al. 1984). Median, mean, and maximum concentrations of antimony in aerosols at three sites in Quebec, Ontario, and Nova Scotia were 0.05-0.10, 0.11-0.23, and 0.37-2.17 ng/m^3, respectively (Hopper and Barrie 1988). According to the Texas Air Control Board, the first- and secondhighest annual average antimony concentration in Texas between 1978 and 1982 was 452 and 50 ng/m3 at Laredo and Dallas, respectively. The statewide 1978-1982 average was below the minimum detectible mean of 90 mg/m^3 (Wiersema et al. 1984).

Concentrations of antimony in 24-hour air samples at Kellogg, Idaho, which is the site of a large and active nonferrous metal industry, ranged from 5.21 to 1,210 ng/m^3 with a mean of 146 ng/m^3 (Ragaini et al. 1977). Air particulate matter in Tacoma, Washington, 40 km downwind of a copper smelter often have antimony concentrations in excess of 300 ppm (Crecelius et al. 1974). The 6-month average concentration of antimony in air in an industrial area of England where a number of ferrous and nonferrous metal smelting and manufacturing works were concentrated was 40 ng/m^3. This is a factor of 50 higher than that found in rural areas (Pattenden et al. 1982). Antimony was reported in air at one site on the NPL (View 1989). The maximum concentration at the site was 69 ng/m^3.

The mean monthly concentration of antimony in precipitation at Birkenes in southern Norway ranged from 0.2 to 2.3 ppb with a mean of 0.6 ppb (Pacyna et al. 1984). During the same period, the respective air concentrations were 0.19-0.80 and 0.43 ng/m^3. Rain samples were collected during two storms upwind and downwind of a copper smelter in Tacoma, Washington. Antimony in rainwater originated primarily from the smelter. The mean total antimony concentration in rainwater downwind from the smelter was 1.3 ppb; the concentration upwind was 0.03 ppb (Vong et al. 1988). Eighty percent of the antimony in rainwater was dissolved (i.e., passed through a 0.45 μm filter).

Antimony is almost entirely found in the particulate, as opposed to the dissolved fraction of snow (Landsberger et al. 1983). The antimony content of

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snow particulate matter in samples from Montreal, Canada, ranged from
4 to 145 ppm. A more recent sampling of snow around Montreal found total
antimony concentrations of l-8.7 ppb and enrichment factors of 39-590
(Zikovsky and Badillo 1987).

Antimony is a component of ammunition, and studies have been performed
to ascertain the elemental concentrations of antimony in the air of indoor
shooting ranges. Antimony might be expected in such situations because it is
alloyed with lead in bullets, and lead stibnite and antimony sulfides are used
as primers (Dams et al. 1988). After an intensive 3-hour shooting exercise,
levels of antimony reached 119 $\mu g/m^3$ or four orders of magnitude over ambient
levels (Vandecasteele et al. 1988). An instructor at the shooting range had a
time-weighted average (TWA) inhalable antimony concentration of 12.0 $\mu g/m^3$,
compared with the threshold limit value (TLV) of 500 $\mu g/m^3$. An American study
conducted at the National Guard Armory in Washington, D.C., during
routine daytime and gun club use, had antimony concentrations ranging from 57
to 216 $\mu g/m^3$ versus background air ranging from 1.5 to 2.3 $\mu g/m^3$, an enrichment
of 9,900 over District of Columbia air) (Olmez et al. 1985). More than 60% of
the antimony was associated with respirable particles with an aerodynamic
diameter less than 3.5 pm.

5.4.2   Water

Antimony has a low occurrence in ambient waters, and there are few
monitoring data with which one can establish a mean value of antimony in
surface waters. Eckel and Jacob (1989) gathered water monitoring data from the
Water Resources Division of the U.S. Geological Survey covering the period
from about 1960 to September, 1988, and found that all but 70 of 1,077 entries
for dissolved antimony were below 5 ppb, which was the probable detection
limit. The geometric mean and standard deviation of the 70 values above 5 ppb
were 12 and 1.93 ppb, respectively. By applying a technique known as
censoring, and assuming a log normal distribution for the monitoring data,
these investigators determined the population geometric mean and standard
deviation for antimony to be 0.25 and 7.16 ppb, respectively. The
concentration of dissolved antimony in other rivers reported in the literature
include: St. Lawrence River at Massena, New York, 1.62 nM (0.197 ppb); Yukon
River 2.73 nM (0.332 ppb); and European rivers less than 0.03-4.43 nM (0.004-
0.539 ppb) (Andreae and Froelich 1984). Few rivers have dissolved antimony
concentrations below 1 nM (0.120 ppb) (Andreae and Froelich 1984).

The major antimony mining area in the United States was the Kellogg
district in northern Idaho, and mining and smelting wastes have been dumped
into the South Fork of the Coeur d'Alene River for over 80 years (Mok and Wai
1990). The South Fork joins with the North Fork of the river to form the Main
Stem of the Coeur d'hlene River somewhat below Kellogg. Mean and maximum total
dissolved antimony concentrations at two sites on the South Fork are 4.3 and
8.2 ppb, respectively. Mean and maximum concentration at six stations on the
Main Stem ranged from 0.6 to 1.0 and 0.8 to 1.9 ppb, respectively.

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Those at a station on the unpolluted North Fork were 0.09 and 0.2 ppb, respectively.

The concentration of dissolved antimony in a polluted estuary in Portugal was found to increase with salinity up to 30 parts per thousand and then rapidly decrease (Andreae et al. 1983). The total antimony content of seawater samples off the Belgian coast ranged from 0.05 to 0.38 ppb (Gillain and Brihaye 1985). Filtered and unfiltered coastal marine waters from the North Adriatic contained 0.31 and 45 ppb, respectively (Strohal et al. 1975).

Little information is available concerning the concentration of antimony in groundwater. The range of antimony concentrations reported for antimony in groundwater in Switzerland (0.3-1.0 ppb) was essentially the same as that reported for the nearby Glatt River (0.5-1.2 ppb) (von Gunten and Kull 1986). The concentration of antimony in groundwater under four retention-recharge basins receiving urban runoff water in Fresno, California, were all less than the 1 ppb detection limit (Nightingale 1987).

Antimony was found in 5.7% and 8.5% of surface waters and groundwaters at hazardous waste sites on the CLPSD (CLPSD 1989). The geometric means of antimony found in positive samples of these media were 40 and 50 ppb, respectively (CLPSD 1989). The CLPSD includes both NPL and non-NPL sites.

Since antimony is used in solder, there has been interest as to whether antimony will leach from pipes soldered with antimony-containing solder into drinking water. Leaching of antimony from tin/antimony (Sn/Sb) solder when it comes in contact with water with pH of 5.2-8.6 was evaluated using loops of pipe containing 20 solder joints (Murrell 1987). Antimony was undetectable (less than 4 ppb) in the water at first, but rose to 10 ppb after 4 days and 68 ppb (at pH 7.4) after 4 weeks. A study was conducted at the University of Washington to evaluate the potential for leaching of metals into drinking water from 95/5 Sn/Sb solder (Herrera et al. 1982). After a series of static and continuous-flow laboratory tests and evaluation of field samples from university buildings, it was concluded that increases in antimony concentration as a result of corrosion and leaching were minimal and would not contribute significantly to dietary antimony intake. Only one of the field samples of standing water from university buildings containing Sn/Sb solder joints was above the detection limit of 0.6 ppb. The sample contained 2 ppb of antimony, one-half of which was dissolved. Examination of the solder joints indicated that a double passivation film of tin monoxide (SnO) and tin dioxide (SnO_2) forms and inhibits leaching.

Sediment is a significant sink for antimony. No information was found on the levels of antimony in pristine sediment. Background antimony concentrations in sediment cores from open water of Lake St. Clair ranged from 0.032 to 0.098 ppm with a mean concentration of 0.061 and 0.068 ppm in sand and silty-clay sediment, respectively (Rossmann 1988). The range of antimony levels in 10 sediments obtained from all over the United States by workers

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engaged in research on contaminated, dredged sediment was 0.5-17.5 ppm, and the median concentration was 2.9 ppm (Brannon and Patrick 1985). Sediment samples taken from Puget Sound in Washington (the site of a copper smelter) were analyzed for antimony. This was the only known anthropogenic source of antimony in the area. While the antimony concentration in sediment from noncontaminated areas ranged from 0.3 to 1.0 ppm, these levels rose to 2-3 times background within 8-15 km of the smelter, and up to 12,500 ppm within 1 km of the smelter where considerable amounts of slag were dumped (Crecelius et al. 1975). One hundred and seven core samples of sediment were collected in the delta area of the Coeur d'Alene river in northern Idaho, a primary antimony mining and smelting area in the United States. The sediment was mostly fine silt, which is typical of mine tailings. The top layer of sediment contained 270-900 ppm of antimony with a mean of 512 ppm (Maxfield et al. 1974). More recent monitoring data reported antimony concentrations in sediment of 137, 49-72, and 1.9 ppm on the South Fork, Main Stem, and North Fork of the Coeur d'Alene River, respectively (Mok and Wai 1990). The South Fork receives mining and smelting wastes, and the North Fork is essentially uncontaminated. A sediment profile on one sample showed that the antimony concentration decreased with depth and was between 2 and 3 ppm between 8.5 and 21.5 cm depth.

5.4.3 Soil

A survey of soils throughout the conterminous United States conducted by the U.S. Geological Survey showed that antimony concentrations ranged from less than 1 to 8.8 ppm with an average concentration of 0.48 ppm. This was the third lowest concentration of the 50 elements surveyed (Shacklette and Boerngen 1984). In this survey, samples were taken at a depth of 20 cm at 1,318 sampling sites. Soils not derived from ore-bearing rock or close to industrial sources do not generally contain more than 1 ppm of antimony. Antimony concentrations in igneous rock, shales, limestone, and sandstone have been reported to be 0.2, 1.5, 0.2, and 0.05 ppm, respectively (Ainsworth 1988). Antimony concentrations in 57 sludge-treated soils in an agricultural area west of Toronto in Ontario, Canada, ranged from 0.16 to 0.37 ppm (dry weight) (Webber and Shamess 1987).

A study of the effects of an antimony smelter on soil found that antimony levels exceeding 50 ppm were found only within 2 km of the smelter (Ainsworth 1988); the background antimony concentration was 6.9 ppm. Antimony concentrations in surface soil near the Kellogg Valley, Idaho, the site of one of the nation's largest and richest mining districts, were considerably elevated at seven contaminated sites, with mean and maximum levels of 111 and 260 ppm, respectively (Ragaini et al. 1977). These values represent an enrichment of 1,000 or more over crustal antimony levels. The concentration profiles in core samples sharply decreased with depth. This indicates that the antimony contamination resulted from air deposition. Soil samples taken in Tacoma, Washington, 40 km downwind of a copper smelter, often

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had antimony concentrations in the range of 11-109 ppm (dry weight). Natural levels are believed to be 3-5 ppm (Crecelius et al. 1974).

The range of maximum antimony concentration in soil at sites on the NPL was 0.084-2,550 ppm (View 1989). The geometric mean and the maximum concentration of antimony found in soil at hazardous waste sites on the CLPSD is 8.0 and 330 ppm, respectively (Eckel and Langley 1988). Thirteen percent of sites on an updated version of CLPSD contain antimony in soil (CLPSD 1989). The geometric mean of positive samples is 17 ppm. The CLPSD includes both NPL and non-NPL sites. The concentration of antimony in surface soil at the Sapp Battery Superfund site in northern Florida, which housed a facility for recovering lead from auto batteries from 1970 to 1980, ranged from 0.46 to 857.0 ppm (Trnovsky et al. 1988).

A New Zealand study showed that the mean level of antimony in street dust was comparable to that in soil (4.69 ppm versus 5.94 ppm) (Fergusson et al. 1986). The antimony content of household dust, however, was enriched approximately two-fold to 10.0 ppm.

5.4.4   Other Environmental Media

A determination of nutrients in a human diet was conducted by the U.S. Food and Drug Administration (FDA) using mixed diet composites representative of the intake of a 25- to 30-year-old U.S. male. The average concentration of antimony in the diet was 9.3 ppb (dry weight). This corresponds to a daily dietary intake of 4.6 μg of antimony assuming a 3,075 g diet/day (wet weight with a total dry matter of 16.2%) (Iyengar et al. 1987). Another study of antimony in food using a highly sensitive neutron activation procedure found that the average antimony concentration in 12 table-ready foods ranged from 0.22 to 2.81 ppb (Cunningham 1987). The food items used in the study were primarily prepared for FDA's Total Diet Studies program in Kansas City and included meats, vegetables, and seafood. The mean concentration ranges of antimony in meats, seafoods, and vegetables were 0.46-1.15, 0.22-1.81, and 1.09-2.81 ppb, respectively. The results of an earlier investigation of trace elements in food in an FDA basket survey reported that median levels of antimony in eight food groups were less than 10 ppb (wet weight) (Tanner and Friedman 1977). In a separate study, the concentration of antimony in pooled human milk was 13 ppb (dry weight) (Iyengar et al. 1982).

In a comprehensive survey of the presence of heavy metals in sewage sludge, 30 sludge samples from 23 American cities were analyzed (Mumma et al. 1984). The antimony concentration in the sludge samples ranged from 1.3 to 55.7 ppm (dry weight) and had a median value of 7.35 ppm. The highest concentration of antimony was in a sludge sample from Baltimore. This level was more than double that of the second highest sludge sample analyzed. In comparison with the above values, the concentration of antimony in cow manure was 0.43 ppm.

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The concentration of antimony in grass from representative sites in the Kellogg Valley, Idaho (the site of the heavy-metal industry), ranged from 6.2 to 111 ppm. Grass from background sites in the valley that were located 3.3 and 7.8 miles from a smelter contained from 3.5 to 4.5 ppm of antimony (Ragaini et al. 1977). Similar results were found around an antimony smelter in England. The antimony content of grass close to the smelter was 50-300 ppm. The content at control sites ranged from 0.1 to 0.3 ppm (Ainsworth 1988). In comparison with the above values, the concentration of antimony in forage crops was about 0.1 ppm (Ragaini et al. 1977).

Concentrations of antimony in selected species of algae, mollusc tissue, crustacean tissue, and fish muscle from southeastern Australia were 0.094-0.193, 0.031-0.060, 0.018-0.116, and less than 0.009-0.010 ppm (dry weight), respectively. The water collected at the site contained 0.17 ppm of antimony (Maher 1986).

A French study of the metallic content in soaps, shampoos, body oils, and cosmetics found that of all products tested only lacquer contained significant amounts of antimony (1.7 ppm) (Demanze et al. 1984). Antimony was found in high concentrations in certain composite resins used in dentistry. Two materials analyzed in England had mean antimony levels of 288 and 403 ppm (Molokhia and Lilley 1986).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Antimony occurs naturally in the earth's crust, and the general population is exposed to low levels of antimony in ambient air and food. The average daily intake of antimony from food or water was estimated at 100 µg/day (Wiersema et al. 1984). According to the recent results of Iyengar (1987), the average daily dietary intake is 4.6 µg, ,and, because of the low antimony levels in water, the average daily intake of antimony (by ingestion) is probably not much greater than 5 pg. Laredo, Texas, has the highest annual average concentration of antimony in ambient air (452 ng/m^3). If a person is assumed to inhale 20 m^3 of air/day, this would amount to an average antimony intake of 9.0 µg/day. For a city such as Washington, D.C. (average antimony concentration about 2 ng/m^3), the inhalation intake would be 0.04 µg/day. Only in an extreme situation would the amount of antimony inhaled compare to the amount that is ingested; the amount inhaled is generally much less. Those people who reside near industrial sources of antimony such as smelters, coalfired power plants, and refuse incinerators are exposed to higher levels of atmospheric antimony. People who spend time in shooting galleries are also exposed to higher antimony levels.

EPA does not believe that the antimony found in such consumer products as car batteries and flame retardants in plastics and textiles results in significant consumer exposure (EPA 1983a). When antimony oxide is used as a fire retardant, it is tightly bound into the material; release and subsequent exposure during use is unlikely (EPA 1983a). No antimony leached from several

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glass containers used for injectable solutions into distilled water, saline, sodium bicarbonate solution, or hydrochloric acid (Pradeau et al. 1988). This glass contained up to 5 ppm of antimony, and the detection limit for the analytical procedure was 10 ppb. In another study, no antimony was detected in water (pH 3, 7, or 10) kept in a canteen for 24 hours (Augustson 1976).

A National Occupational Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983 estimated that 373,460 workers were potentially exposed to antimony (molecular formula unknown) in the United States in 1981-1983 (NIOSH 1989). The number of workers exposed to antimony trioxide, antimony sulfide, antimony oxide, antimony pentoxide, antimony dialkyldithiocarbamate, and other antimony compounds is estimated to be 226,645. The total estimated number of workers exposed to antimony and all of its compounds is 486,347. Since all of the data for trade-name products that may contain antimony have not been analyzed, this estimate is preliminary. The NOES was based on field surveys of 4,490 facilities. It was designed as a nationwide survey based on a statistical sample of virtually all workplace environments in the United States where eight or more persons are employed in all standard industrial codes (SIC) except mining and agriculture. The NOES database does not contain information on the frequency, concentration, or duration of exposure of workers to any of the chemicals listed therein. These surveys provide only estimates of the number of workers potentially exposed to chemicals in the workplace. EPA states that the NOES figures substantially overestimate occupational exposure to antimony and compounds (EPA 1983a). Most antimony in this country is either smelted from imported ore or impure metallic antimony or recycled from antimony scrap. According to EPA, "mining, hauling, and crushing of ore will be of minor consequence," because ore crushing is done in closed systems, and ore processing is done under wet conditions to minimize dust (EPA 1983a). Following a membership survey, the Antimony Oxide Industry Association (AOIA) reported that 230-240 production workers and l,000-2,000 workers using antimony were exposed to antimony (EPA 1983a). This represented the entire population.of workers potentially exposed to antimonial substances. An independent survey of the three facilities producing and processing antimony metal in 1979 estimated that 2,249 workers were exposed to antimony (EPA 1983a). This estimate included producers and first-level processors of antimony metal into products such as batteries and alloys. Alloys usually contain small amounts of antimony that are most often combined with much larger amounts of lead. Occupational exposure controls that are employed to mitigate lead exposure also protect workers from antimony. Much of the estimated exposure to antimony metal may actually be to antimony oxide; fumes formed when heating the metal (e.g., for carting) are oxidized. The survey also estimated that 1,710-1,880 workers were employed at facilities that manufacture and process antimony trioxide. EPA believes that 200-2,000 workers may be exposed to stibnite, which is used in small quantities in smokes and in priming mixtures for igniting explosives (EPA 1983a). This stibnite is expected to form antimony trioxide during use, and exposure will be primarily to the oxide.

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There have not been any systematic and representative surveys of occupational exposure levels to antimony in industry; however, some data are available from walk-through surveys of selected companies conducted by NIOSH and other investigators. In some of these surveys, only a few samples were analyzed. In a facility where antimony oxide was produced from the sulfide ore, breathing-zone samples from five antimony oxide production workers ranged from 0.21 to 3.2 mg antimony/m^3; four of these samples were above 0.5 mg antimony/m^3. Air samples from the bagging area ranged from 0.43 to 0.83 mg antimony/m^3 (Cassady and Etchison 1976). In another facility that produced antimony and antimony oxide from ore, breathing-zone samples from 55 employees ranged from 0.05 to 6.21 mg antimony/m^3, and area air samples ranged from 0.14 to 2.12 mg antimony/m^3 (Donaldson 1976). The mean exposure for the antimony oxide operation was 2.23 mg/m^3, and this was the highest in the plant. Two personal air samples in a third antimony oxide production facility were 2.7 and 5.0 mg antimony/m^3, and general area samples ranged from 1.8 to 5.6 mg antimony/m^3 (Donaldson and Gentry 1975). In a secondary lead smelter where scrap batteries were reclaimed, breathing zone samples in 2 of 21 workers were quantifiable; these TWAs were 0.037 and 0.051 mg/m^3 (Craig et al. 1981). TWA antimony concentrations in the compounding area of a rubber company ranged from 0.01 to 0.15 mg/m^3, and the mean in an iron foundry was 0.00015 mg/m^3 (Salisbury 1980; Zhang et al. 1985). Antimony levels in a glass production facility were 0.005 mg/m^3, and this represents 1% of the NIOSH-recommended maximum level (Burroughs and Horan 1985). Antimony may also be released during injection molding of ignitionresistant polystyrene in which fire retardant additives that contain antimony are used. In one such study, antimony levels ranged from less than the detection limit of 0.0003 to 0.2 mg/m^3 (Willetts et al. 1982).

Since antimony trioxide is used in many materials as a fire retardant, it is likely that antimony will be released during fires. Antimony was present in soot and in tracheal specimens of people who perished in fires (Willetts et al. 1982). In 18 cases that were analyzed, soot antimony concentrations ranged from 0.1 to 543 ppm, and 50% of tracheal antimony concentrations exceeded the normal range of 0.1-124.0 ppm. These results indicate that firemen and other people at fires may be exposed to increased antimony levels in smoke.

Stibine may be produced in lead-acid battery plants during the formation process (Jones and Gamble 1984). In a study involving five battery plants, stibine concentrations ranged from not detectable to 2.5 mg/m^3. In three other surveys of battery plants, stibine concentrations ranged from not detectable to 0.35 mg/m^3 (Young 1979a), 0.007 mg/m^3 (Young 1979b), and 0.031 mg/m^3 (Young et al. 1979). Stibine was also reported in a company that manufactured glass for hypodermic syringes at levels up to 0.5 mg/m^3 (Burroughs and Horan 1985).

Antimony trioxide is used in the glass industry as a refining agent and colorant. In an exposure assessment in the German glass industry, TWA

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antimony levels were as high as 0.351 mg/m^3 (Ludersdorf et al. 1987). Urine and blood antimony levels of exposed workers were enhanced. The median and maximum urine antimony levels in spot urine samples were 1.9 and 15.7 µg/L, respectively, compared with 0.4 and 0.7 µg/L for controls. Median and maximum blood levels for workers were 1.0 and 3.1 µg/L, respectively, versus 0.3 and 1.7 µg/L, respectively, for unexposed persons.

Nail samples from 71 Americans contained an average of 0.41 ppm of antimony. Averages for residents of four other countries ranged from 0.28 to 0.70 ppm (Takagi et al. 1988). In an analogous study, the mean concentration of antimony in hair samples from 55 men and women from Scranton, Pennsylvania, contained 0.096 ppm of antimony. The hair samples of populations from cities in four other countries contained mean antimony levels between 0.11 and 0.86 ppm (Takagi et al. 1986). These hair levels can also be compared to those in a Japanese national study in which the geometric mean concentration and standard deviation of antimony in washed hair samples from 234 healthy individuals were 0.078 and 2.5 ppm, respectively. No significant differences between different sexes or age groups were noted (Ohmori et al. 1981). In another Japanese study, hair and nail samples taken from workers at an antimony refinery, nearby residents, and a control group were analyzed before and after washing with a nonionic, surface-active agent in an ultrasonic cleaner (Katayama and Ishide 1987). The concentration of antimony in the nails of the three groups before and after washing was 730, 2.46, 0.19 ppm and 230, 0.63, and 0.09 ppm, respectively. The concentration of antimony in the hair of workers before and after washing was 222 and 196 ppm, compared with 0.21 and 0.15 ppm for controls. Exposure to antimony, therefore, greatly increases the antimony levels in nails and hair. The concentration in nails in exposed people is largely surficial.

A group of 21 workers from northern Sweden who were employed in nonferrous metal smelting and refining industries had median antimony concentrations' in their lungs of 0.30 ppm (wet weight). Controls from an unpolluted area had 0.029 ppm in their lungs (Hewitt 1988). Antimony concentrations in the lung tissues of eight British coal miners ranged from 0.19 to 0.59 ppm (dry weight); the levels in two controls were 0.47 and 0.62 ppm (Hewitt 1988).

5.6   POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In discussing exposure to antimony, it is important to consider what form of antimony a person is exposed to and what is its availability. Such information is seldom available. Although high concentrations of antimony may be found in contaminated soil and sediment, the few studies that have been conducted indicate that much of the antimony may be embedded in a crystalline matrix or bound to hydrated iron, aluminum, and manganese oxides. In water, the pentavalent state is predominant, although significant levels of trivalent antimony and methylated antimony compounds exist. People who live or work near sources of antimony such as smelters, coal-fired power plants, and refuse

incinerators may be exposed to high levels of antimony in airborne dust, soil, and vegetation. People who live near or work at waste sites that receive slag from smelters or fly ash from power plants and refuse incinerators may also be exposed to higher than background levels. Exposure routes would include either inhalation of contaminated air or ingestion of contaminated soil or vegetation. Similarly, people who are exposed to soot and smoke in fires, such as firemen, may be exposed to high levels of antimony. Occupational exposure to antimony appears to be highest for those involved in the production and processing of antimony and antimony oxide. Workers in battery-forming areas of lead-storage battery plants may be exposed to high levels of stibine.

5.7   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 antimony is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (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 antimony.

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 or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1   Data Needs

Physical and Chemical Properties. It is apparent from the physical and chemical properties of antimony and antimony trioxide shown in Table 3-2, that there are discrepancies in the literature values for the boiling points of antimony, antimony trichloride, and antimony trioxide (Freedman et al. 1978; Herbst et al. 1985; Weast 1988; Windholz 1983). This may be due to different levels of impurities in the samples tested. The fact that no numerical value exists for the water solubility of antimony trioxide, antimony pentoxide, and antimony pentasulfide is of no special significance. For inorganic salts, the solubility product coupled with stability constants for the ionic species in solution are the factors determining how much of the compound.goes into solution; the solubility in terms of the number of milligrams of the parent compound in solution, as used for organic compounds, is not meaningful. We do not know whether all the solubility products and stability constants for antimony and its compounds, required for determining the antimony species in natural water and their concentrations, are available. Other physical and

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chemical properties in Table 3-2 for which there are no data are generally not well defined for antimony and its compounds or are not useful in determining their environmental fate.

Production, Import/Export, Use, and Disposal. Information on the production, import, and use of antimony and antimony trioxide is readily available (Carapella 1978; Llewellyn 1988; Plunkert 1982; U.S. Bureau of Mines 1989a). However, information on the production, import, and use patterns of other antimony compounds is not available, and is needed to assess human exposure to these compounds. Except for the recycling of batteries, little information is available concerning the disposal of antimony and its compounds.

Much of the antimony released to the environment is transferred to offsite locations for disposal (probably landfills) (TRI 1989). Most of the waste products from mining and smelting operations are discarded on land in large tailing piles; many of these are now abandoned (TRI 1989). Acid conditions are often created in these tailing piles by the oxidation of pyrites contained in the tailings that increase the potential for leaching (DeLaune and Smith 1985). Information concerning antimony leaching from slag heaps is important in assessing antimony releases to the environment. More detailed information regarding the form of antimony that is disposed of and the disposal methods is necessary to assess the potential exposure to these compounds.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxic Release Inventory (TRI), which contains this information for 1987, became available in May of 1989 (TRI 1989). This database will be updated yearly and should provide a list of industrial production facilities and emissions. Releases according to this database are shown in Table 5-l.

Environmental Fate. In assessing human exposure, the form (valence state, compound, adsorption, coprecipitation, particle size) of antimony and its availability must be considered. This information is apt to be sitespecific. Data concerning the forms of antimony in air, soil, water, and sediment are limited. Information regarding the transformations that may occur, the rates of transformation, and the conditions that facilitate the transformations is also lacking. For example, we do not know whether antimony is methylated in soil as is arsenic and as antimony itself may be methylated in the aquatic environment (Andreae et al. 1983; Austin and Millward 1988). Information relating to the adsorption of antimony and its compounds by soil and sediment is limited. This information should cover a range of soil types, soil components (e.g., clay), and conditions.

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Bioavailability from Environmental Media. Antimony is poorly absorbed following inhalation and oral exposure (Felicetti et al. 1979a, 1979b; Gerber et al. 1982; Thomas et al. 1973). Dermal exposure to high levels of antimony trioxide resulted in death in rabbits (Myers et al. 1978). The application area was occluded, suggesting that at least some forms of antimony can be absorbed through the skin. Although there is no information on the absorption efficiency of antimony from environmental media in humans, there is evidence in animals that it is absorbed. The vegetation and soils at sites near antimony smelters are heavily contaminated with antimony. Elevated levels of antimony in various tissues were observed in animals living near the smelter (Ainsworth 1988). An animal study designed to measure the rate of absorption of antimony from environmental media would be useful in assessing the toxicological significance of levels of antimony in the air and soil near hazardous waste sites.

Food Chain Bioaccumulation. Extensive studies at a smelter site indicate that the uptake of antimony from soil in grass and subsequent translocation in shoots is slight (Ainsworth 1988). At a polluted site, most of the antimony on plants resulted from atmospheric deposition. These studies additionally showed that there was no bioaccumulation of antimony in small mammals compared with their food. Other studies on fish and aquatic organisms indicate that the bioconcentration of antimony is low (Callahan et al. 1978; EPA 1980; Maher 1986). Accordingly, there is little indication that antimony would bioconcentrate in the food chain and in humans. It should be pointed out that data on the biconcentration of antimony in fish and biomagnification in higher trophic levels of animals is limited. Monitoring data on the levels of antimony in plants and animals is minimal. A larger database of information covering more sites and species is desirable. This would establish whether antimony might accumulate in some species or in the presence of some forms of antimony.

Exposure Levels in Environmental Media. Although some data on the levels of antimony in ambient air are available, these data are not representative and recent enough to estimate the current exposure levels to antimony by the U.S. population via inhalation (Austin and Millward 1988; Hopper and Barrie 1988; Johnson et al. 1984; Kowalczyk et al. 1982; Schroeder et al. 1987; Wiersema et al. 1984). While the levels of antimony in water are generally very low (Eckel and Jacob 1989), the data for ambient water are marginally adequate; data for drinking water and groundwater are virtually nonexistent. Similarly data regarding the levels of antimony in the various food classes and diet are fragmentary (Cunningham 1987; Syengar et al. 1987; Tanner and Freedman 1977). Reliable and recent monitoring data for antimony in air, water, and foods are essential for estimating the extent of exposure from each of these sources. While the levels of antimony in surface and groundwater at hazardous waste sites are elevated above ambient levels (CLPSD 1989), the elevation is not very great. Since it is not clear whether the levels reported at waste sites are for dissolved antimony as are the ambient

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levels, the difference between antimony concentrations at waste sites and ambient sites may be lower. Antimony concentrations in soil at some hazardous waste sites are high (CLPSD 1989; Eckel and Langley 1988; View 1989), and there is a potential of exposure from ingesting soil at these sites. The leaching potential of these soils appears to be low (Ainsworth 1988; Foster 1989; King 1988; Trnovsky et al. 1988). The exposure potential from antimony at these sites from antimony reentrained by wind also appears to be low (Ainsworth 1988).

Exposure Levels in Humans. The levels of antimony in the hair, nails, and breast milk of a sample of the U.S. population are known (Iyengar et al. 1982; Takagi et al. 1986, 1988). While the tissue levels of antimony in Japanese people are available (Sumino et al. 1975), analogous levels for Americans were not found. In particular, no reliable data regarding the levels of this element in the blood and urine of unexposed U.S. residents are available. Such data may be helpful in establishing the background exposure levels of antimony. Levels of antimony in hair, nails, lung, blood, and urine of some exposed workers are available, but the amount of data is small (Hewitt 1988; Katyama and Ishidi 1987; Ludersdorf et al. 1987). None of these data refer to populations living around the hazardous waste sites containing elevated levels of antimony. Such data may be significant in assessing the exposure levels of this component of the population.

Exposure Registries. No exposure registries for antimony and its compounds were located. Antimony and its compounds do not currently have a subregistry established in the National Exposure Registry. They 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 the exposure to the compound.

5.7.2   On-going Studies

Remedial investigations and feasibility studies conducted at the 52 NPL sites known to be contaminated with antimony will add to the available database on exposure levels in environmental media, exposure levels in humans, and exposure registries, and will increase the current knowledge regarding the transport and transformation of antimony in the environment. NIOSH is updating its estimates of occupational exposure by including exposure to antimony and its compounds in trade name chemicals (NIOSH 1989). No other ongoing research studies pertaining to the environmental fate of antimony or to occupational or general population exposures to antimony were identified.