

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Silver is a rare element, which occurs naturally in its pure form as a white, ductile metal, and in ores. It has an average abundance of about 0.1 ppm in the earth's crust and about 0.3 ppm in soils. There are four oxidation states (0, 1+, 2+, and 3+); the 0 and 1+ forms are much more common than the 2+ and 3+ forms. Silver occurs primarily as sulfides, in association with iron (pyrite), lead (galena), and tellurides, and with gold. Silver is found in surface waters in various forms: (1) as the monovalent ion (e.g., sulphide, bicarbonate, or sulfate salts); (2) as part of more complex ions with chlorides and sulfates; and (3) adsorbed onto particulate matter.

Silver is released to air and water through natural processes such as the weathering of rocks and the erosion of soils. Important sources of atmospheric silver from human activities include the processing of ores, steel refining, cement manufacture, fossil fuel combustion, municipal waste incineration, and cloud seeding. The total U.S. annual release of silver to the environment as a result of human activities in 1978 was estimated to be approximately 2 million kg. Of this amount, 77% was from land disposal of solid waste, 17% was discharged to surface waters, and 6% emitted to the atmosphere. Ore smelting and fossil fuel combustion emit fine particles of silver that may be transported long distances and deposited with precipitation. The major source of release to surface waters is effluent from photographic processing. Releases from the photographic industry and from disposal of sewage sludge and refuse are the major sources of soil contamination with silver. Sorption is the dominant process controlling partitioning in water and movement in soil. Silver may leach from soil into groundwater; acidic conditions and good drainage increase the leaching rate. Silver is bioconcentrated to a moderate extent in fish and invertebrates.

The general population is exposed to silver primarily through the ingestion of drinking water and food. The most recent estimate by NIOSH indicates that about 70,000 people are potentially exposed to silver in workplace environments in the United States. Inhalation is probably the most important route of occupational exposure. Populations with exposure to higher than background levels of silver include workers in industries processing or using the compound and members of the general public who consume drinking water or food containing elevated levels of silver. Sources of elevated dietary silver include seafood from areas near sewage outfalls or industrial sources and crops grown in areas with high ambient levels of silver in the air or soil.

According to the VIEW Database (1989), silver has been found at 27 sites on the National Priority List of 1,177 sites. The frequency of these sites

5. POTENTIAL FOR HUMAN EXPOSURE

within the United States can be seen in Figure 5-1. EPA's Contract Laboratory Program (CLP) statistical database indicates that silver has been detected at 100% of the 2,783 Superfund hazardous waste sites that have had samples of all media analyzed by the CLP (CLP 1988).

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

The total U.S. annual anthropogenic release of silver to the atmosphere from production processes and consumptive uses in 1978 was estimated at 77,700 kg (Scow et al. 1981). Of this amount, an estimated 30,000 kg were released from metals production, 22,000 kg from use in electrical contacts and conductors, 9,000 kg from coal and petroleum combustion, 7,000 kg from iron and steel production, 2,000 kg from cement manufacture, and the remainder from miscellaneous uses. Urban refuse was the source of an additional 10,000 kg. Smith and Carson (1977) estimated that cloud seeding with silver iodide contributed 3,100 kg annually (based on data from the early 1970s).

5.2.2 Water

The total U.S. annual release of silver to surface waters in 1978 from production processes and consumptive uses was estimated to be 125,000 kg (Scow et al. 1981). Of this amount, an estimated 65,000 kg were released from photographic developing, 54,000 kg from photographic manufacture, 5,000 kg from metals production, and the remainder from miscellaneous uses. An additional 70,000 kg were estimated to be released from sewage treatment plants, 72,000 kg from urban runoff, and 438,000 kg from natural sources (e.g., soil erosion). Silver released in precipitation as a result of cloud seeding has decreased and is not expected to contribute significant amounts to water (Scow et al. 1981). Leachates containing silver may enter ground waters when tailing ponds or piles are situated in areas with high water tables or when abandoned mines or sections of mines are saturated (Letkiewicz et al. 1984).

Other sources of silver release to surface waters include textile plant wastewater effluent (Rawlings and Samfield 1979); petroleum refinery effluents (Snider and Manning 1982); and quench water and fly ash scrubber water effluents from municipal incinerators (Law and Gordon 1979). Silver was detected in 7 of 58 (12%) samples from the National Urban Runoff Program survey (Cole et al. 1984).

5.2.3 Soil

The total U.S. annual release of silver to land from production processes and consumptive uses in 1978 was estimated at 1.01 million kg (Scow et al. 1981). Of this amount, an estimated 630,000 kg were released from the photographic industry (in manufacture and developing), 165,000 kg from metals

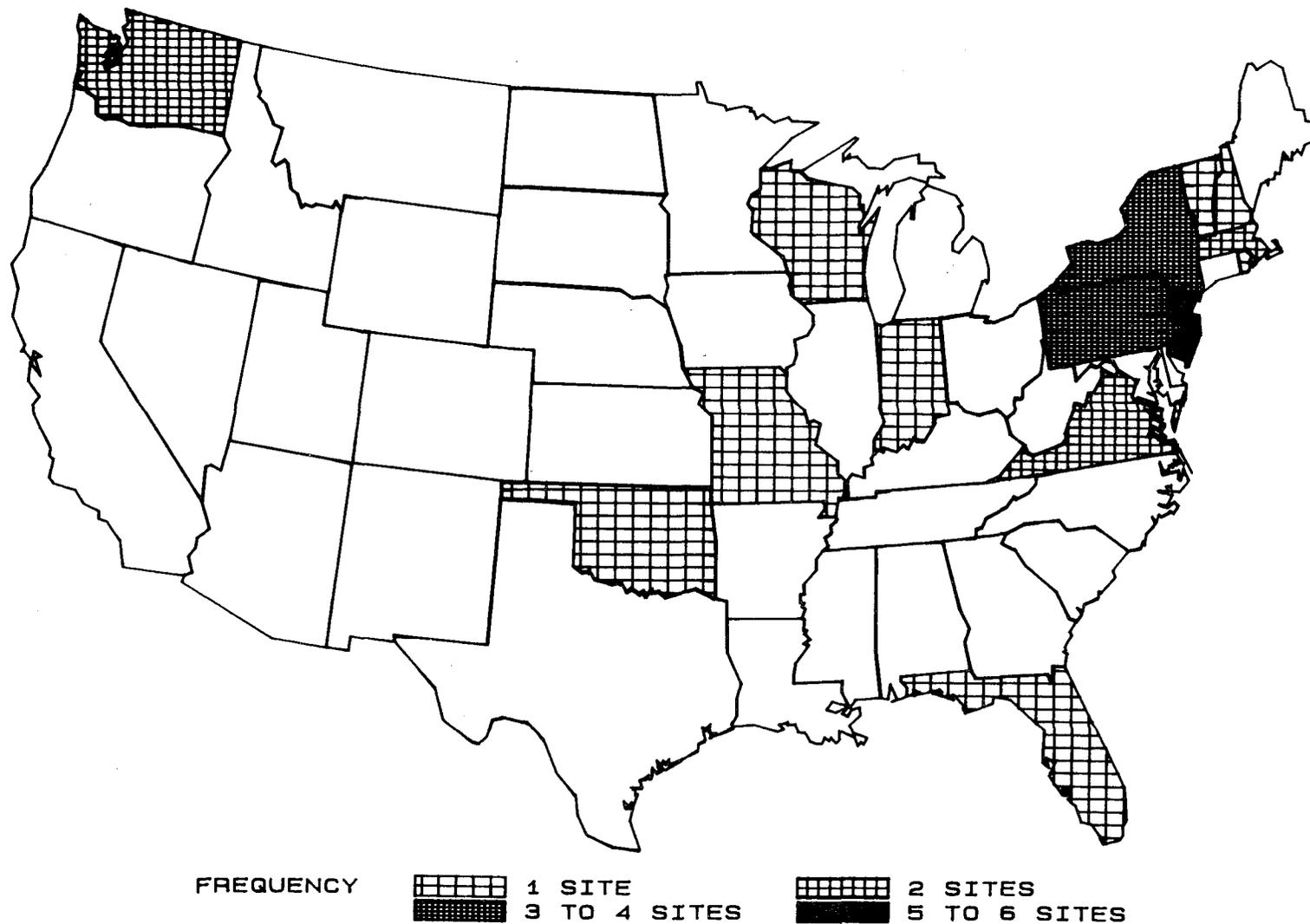


FIGURE 5-1. FREQUENCY OF SITES WITH SILVER CONTAMINATION

5. POTENTIAL FOR HUMAN EXPOSURE

production, 150,000 kg from uses in electrical contacts and conductors, 60,000 kg from uses in brazing alloys and solders, and the remainder from miscellaneous uses. An additional 370,000 to 520,000 kg were estimated to be released from urban refuse and 220,000 kg from sewage treatment. Smith and Carson (1977) estimated that the use of silver containing photographic materials contributed an annual 370,000 kg in sewage sludge; of this amount an estimated 52.5% was placed in landfills, 26.7% was lagooned, and 20.8% was spread on land.

The major source of elevated silver levels in cultivated soils is from the application of sewage sludge and sludge effluents as agricultural amendments. Additional anthropogenic sources of silver in soil include atmospheric deposition (especially from ore processing); landfilling of household refuse, sewage sludge, or industrial wastes; and leaching of metal tailings (Smith and Carson 1977).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

The global biogeochemical movements of silver are characterized by releases to the atmosphere, water, and land by natural and man-made sources, possible long-range transport of fine particles in the atmosphere, wet and dry deposition, and sorption to soil and sediments. The major forms of silver in the atmosphere are probably metallic silver, silver sulfide, silver sulfate, silver carbonate, and silver halides (Smith and Carson 1977). Silver is released to the atmosphere as an aerosol (suspension of solid or liquid particles in a gas such as air). Mining operations such as grinding emit large particles (more than 20 μ diameter) that settle near the source while particles emitted from smelting, fossil-fuel fired power plants, and solid waste incinerators are smaller and are likely to be transported away from the source of release (Scow et al. 1981). Fine particles (less than 20 μ diameter) in the aerosol tend to be transported long distances in the atmosphere and are deposited with precipitation. Long-range atmospheric transport of silver is indicated by several studies in which atmospheric particulate concentrations were elevated above background levels in areas removed from cloud seeding or mining activities (Davidson et al. 1985; Struempfer 1975). Scow et al. (1981) estimated that about 50% of the silver released into the atmosphere from industrial operations will be transported more than 100 km and will eventually be deposited by precipitation.

The transport and partitioning of silver in surface waters and soils is influenced by the particular form of the compound. Lindsay and Sadiq (1979) stated that under oxidizing conditions the primary silver compounds would be bromides, chlorides, and iodides, while under reducing conditions the free metal and silver sulfide would predominate. In water, the major forms of silver are as the monovalent ion in the form of sulfate, bicarbonate, or sulfate salts; as part of more complex ions with chlorides and sulfates; and

5. POTENTIAL FOR HUMAN EXPOSURE

as an integral part of, or adsorbed onto, particulate matter (Boyle 1968). In one study, silver in river water was primarily found in the following forms: silver ion (Ag^+) -- 53-71%, silver chloride (AgCl°) -- 28-45%, silver chloride ion (AgCl_2^-) -- 0.6-2.0% (Whitlow and Rice 1985). Callahan et al. (1979) stated that sorption is the dominant process leading to the partitioning of silver in sediments. Significant quantities of silver in water are sorbed by manganese dioxide; pH and oxidation-reduction conditions affect sorption (Anderson et al. 1973). Kharkar et al. (1968) reported that approximately 90% of the silver in rivers was in a dissolved form and 10% was a suspended solid. Concentrations in lake sediments were reported to be 1000 times that of the overlying waters; the highest content was associated with fine-grained sediments (Freeman 1977).

The mobility of silver in soils is affected by drainage (silver tends to be removed from well-drained soils); oxidation-reduction potential and pH conditions (which determine the reactivity of iron and manganese complexes which tend to immobilize silver); and the presence of organic matter (which complexes with silver and reduces its mobility) (Boyle 1968). The distribution coefficient (K_d : ratio of the concentration in soil to the concentration in water) for silver in a number of soils ranged from 10 to 1,000 (Baes and Sharp 1983). Factors that affect the K_d include soil pH, clay content and particle size distribution, organic matter content, and free iron and manganese oxide content. The enhanced ability of organic matter to immobilize silver is demonstrated by the increased levels of silver found in peat and bog soils and in marshes (Boyle 1968). In pasture plants growing in the vicinity of an airborne source of silver such as a smelter, silver in the leaves is apparently derived from deposition, of airborne silver, while concentrations in the roots are from soil uptake (Ward et al. 1979). Silver levels in the leaves were slightly greater than levels in the roots.

Silver accumulation in marine algae appears to result from adsorption rather than uptake; bioconcentration factors of 13,000-66,000 have been reported (Fisher et al. 1984).

Data on the potential for accumulation of silver has been studied in several aquatic species. Several of these studies do not conform to current bioconcentration test procedures in terms of numbers of fish, duration of exposure, and measurement of concentrations in aquaria. EPA (1980a) reported a bioconcentration factor of less than 1 in bluegills (*Lepomis macrochirus*) exposed to silver nitrate for 28 days. Approximate bioaccumulation factors of 4-6 for bluegill were calculated based on a 6-month study and 2-10 for large mouth bass (*Micropterus salmoides*) exposed to silver nitrate for 4 months (both dry weight) (Coleman and Cearley 1974).

Terhaar et al. (1977) studied bioconcentration (uptake from water) and bioaccumulation (uptake from food and water) of silver thiosulfate complexes in algae (*Scenedesmus* sp.), water flea (*Daphnia magna*), mussels (*Ligumia* sp. and *Margaritifera* sp.), and fathead minnow (*Pimephales promelas*) in 10-week

5. POTENTIAL FOR HUMAN EXPOSURE

exposures. Bioconcentration indices were 96-150 for algae, 12.2-26 for Daphnia, 5.9-8.5 for mussels, and 1.8-28 for fish. Bioaccumulation indices were 9-26 for Daphnia, 6.6-9.8 for mussels, and 4.0-6.2 for fish. These indices, which are based on measured wet weight concentrations in biota and nominal concentrations in water, indicate little potential for silver biomagnification (systematic increase in residue concentrations moving up a food chain) in the tested aquatic food chain.

Bioconcentration factors of 1,055-7,650 (wet weight) were estimated in a 21-month study with the mussel (Mytilus edulis) in salt water (Calabrese et al. 1984). The clam, Macoma balthica, contained silver at 32-133 µg/g (dry weight tissue) in an area of San Francisco Bay near a sewage outfall; background concentrations in this species in the bay were less than 1 µg/g (Thomson et al. 1984). These data indicate that inputs of silver to an estuary are available to sediment-dwelling animals. Silver from sewage sludge at an ocean disposal site was bioaccumulated by the sea scallop (Placopecten magellanicus). Maximum concentrations in scallops located near the disposal site were 9.08 ppm (dry weight tissue) while scallops located away from the site had levels less than 1 ppm (Pesch et al. 1977). The estimated biological half-lives for the elimination of silver were 26.4 days for the Pacific oyster (Crassostrea gigas) and 149.1 days for the American oyster (C. virginica) (Okazaki and Panietz 1981).

5.3.2 Transformation and Degradation

5.3.2.1 Air

Particulates of metallic silver emitted from the burning of fossil fuels and municipal refuse are likely to become coated with silver oxide, silver sulfide, and silver carbonate as the particles cool and undergo deposition (Smith and Carson 1977).

5.3.2.2 Water

In fresh water, silver may form complex ions with chlorides, ammonium (in areas of maximum biological activity), and sulfates; form soluble organic compounds such as the acetate and the tartrate; become adsorbed onto humic complexes and suspended particulates; and become incorporated into, or adsorbed onto, aquatic biota (Boyle 1968). Where decaying animal and plant material are abundant, silver strongly precipitates as the sulfide or combines with humic materials (Smith and Carson 1977).

5.3.2.3 Soil

Silver tends to form complexes with inorganic chemicals and humic substances in soils (Boyle 1968). Since silver is toxic to soil microorganisms and inhibits bacterial enzymes (Domsch 1984), biotransformation is not expected to be a significant process.

5. POTENTIAL FOR HUMAN EXPOSURE

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Silver was measured in particulate samples from rural and urban areas both adjacent to and removed from activities such as metal smelting, refining, and silver iodide cloud seeding. Background levels appear to be less than 1 ng/m³ as evidenced by the measurement of average silver concentrations of 0.018 ng/m³ at Great Smoky Mountains National Park; 0.012 ng/m³ at Olympic National Park; and less than 0.19 ng/m³ at Glacier National Park (Davidson et al. 1975). The highest particulate levels (mean -- 10.5 ng/m³; range -- 0.936-36.5 ng/m³) were measured in Kellogg, Idaho (in the Coeur d'Alene River Basin) near a large smelter complex (Ragaini et al. 1977). In an industrialized area of northwest Indiana, silver was measured at less than 1-5 ng/m³ (Harrison et al. 1971). A level of 1 ng/m³ was reported by Douglas (1968) in a rural cloud-seeding target area. In a rural area of Nebraska where no cloud seeding was known to have occurred, Struempfer (1975) found particulate silver concentrations averaged 0.04-0.15 ng/m³ during three sampling periods. This researcher theorized that anthropogenic sources, such as long-range transport from cloud seeding, were responsible for the enrichment of silver by factors of 326-355 over its average concentration in the earth's crust. Silver concentrations in precipitation resulting from seeding clouds with silver iodide were 10-4500 ng/L compared with concentrations of 0-20 ng/L without cloud seeding (Cooper and Jolly 1970).

5.4.2 Water

Boyle (1968) reported average (background) ambient concentrations of silver in fresh waters of 0.2 µg/L and in sea water of 0.25 µg/L. Waters that leach silver-bearing deposits (e.g., in mining areas) may carry up to 100 times more silver than other fresh waters (Scow et al. 1981). Leaching is enhanced by low pH (Smith and Carson 1977). In samples of 170 lakes in California, silver concentrations averaged 0.1 µg/L with a maximum of 6.0 µg/L (Bradford et al. 1968). Kharkar et al. (1968) reported that the average silver concentration of 10 U.S. rivers was 0.30 µg/L (range: 0.092-0.55 µg/L). In another survey, Kopp (1969) found silver in 6.6% of 1,577 surface waters sampled with a mean detected concentration of 2.6 µg/L (range: 0.1-38 µg/L). For 1970-1979, according to U.S. surface water sampling data from EPA's STORET database, the annual mean levels ranged from 1 µg/L to 9 µg/L and annual maximum concentrations were 94 µg/L to 790 µg/L (Scow et al. 1981). In 10 out of 13 major U.S. river basins, silver concentrations decreased from 1975-1979 as compared with 1970-1974. Concentrations increased in the North Atlantic, Southeast, and Lower Mississippi basins. In the U.S. Geological Survey, Water Resources Division portion of the database (from the early 1960s to mid-1988), silver was detected in 2,195 of over 10,000 surface water samples; the mean and median concentrations in these samples were 1.9 µg/L and 2.0 µg/L, respectively (Eckel and Jacob 1988).

5. POTENTIAL FOR HUMAN EXPOSURE

Hem (1970) reported a median silver concentration of 0.23 $\mu\text{g/L}$ in U.S. drinking water. Letkiewicz et al. (1984) analyzed the results of three surveys of U.S. groundwater and surface water used as drinking water supplies. These surveys were the 1969 U.S. Public Health Service Community Water Supply Survey (CWSS 1969), the 1978 EPA Community Water Supply Survey (CWSS 1978), and the 1978 through 1980 EPA Rural Water Survey (RWS). In CWSS 1969, silver was detected (minimum positive value was 0.1 $\mu\text{g/L}$) in 309 of 677 groundwater supplies, (mean 1.7 $\mu\text{g/L}$, median 1.3 $\mu\text{g/L}$, and range 0.1 to 9 $\mu\text{g/L}$). Silver was detected in 59 of 109 surface water supplies with a mean and median of 1.3 $\mu\text{g/L}$ and a range of 0.1 to 4 $\mu\text{g/L}$. In CWSS 1978, silver was detected (minimum positive value was 30 $\mu\text{g/L}$) in 8 of 81 groundwater supplies (range 30-40 $\mu\text{g/L}$, mean 31.9 $\mu\text{g/L}$, and median 30 $\mu\text{g/L}$). Silver was found in 4 of 25 surface water supplies (range 30-40 $\mu\text{g/L}$, mean 36.2 $\mu\text{g/L}$, and median 37.5 $\mu\text{g/L}$). In the RWS conducted between 1978 and 1980, silver was detected (minimum quantifiable concentration apparently was 20 $\mu\text{g/L}$) in 10 of 71 groundwater supplies (mean and median 40 $\mu\text{g/L}$ and range 20-80 $\mu\text{g/L}$). Silver was detected in 8 of 21 surface water supplies. The range, mean, and median of these 8 supplies were 20-60 , $\mu\text{g/L}$, 36.2 $\mu\text{g/L}$, and 35 $\mu\text{g/L}$, respectively. Letkiewicz et al. (1984) also summarized information from EPA's Federal Reporting Data System as of 1984, which indicated that 14 public water supplies (13 from groundwater) in the United States reported silver levels above 50 $\mu\text{g/L}$. Letkiewicz et al. (1984) stated that it is not possible to determine which of these surveys is representative of current levels of silver in the U.S. water supply. The large range in apparent detection limits further limits the usefulness of these data in estimating silver levels in U.S. water supplies.

Silver has been detected with a geometric mean concentration of 6.0 $\mu\text{g/L}$ in groundwater samples from 613 of the 2,783 (22%) hazardous waste sites included in EPA's Contract Laboratory Program (CLP) statistical database (CLP 1988). It has also been detected in surface water samples from 552 of the 2,783 (20%) sites in the CLP statistical database with a geometric mean concentration of 9.0 $\mu\text{g/L}$ (CLP 1988).

5.4.3 Soil

From a series of measurements in Canada, Boyle (1968) estimated that the average silver content of soils (except for mineralized zones such as mining areas) was 0.30 ppm and the average abundance in the earth's crust was 0.10 ppm . The major source of elevated silver levels in cultivated soils is from the application of sewage sludge and sludge effluents (Smith and Carson 1977). The average silver concentration in soils near a lead smelting complex in Kellogg, Idaho (in the Coeur d'hlene River Basin) was 20 ppm (range: 3.2-31 ppm) (Ragaini et al. 1977). Klein (1972) measured soil metal concentrations in the Grand Rapids, Michigan area in order to examine possible relationships between concentrations and land use. Silver concentrations in soils that were classified by land use were 0.13 ppm (residential), 0.19 ppm (agricultural), and 0.37 ppm (industrial) (Klein 1972).

5. POTENTIAL FOR HUMAN EXPOSURE

The Contract Laboratory Program (CLP) statistical database indicates that silver has been detected with a geometric mean concentration of 4.5 ppm in soil samples from 1,807 of 2,783 (65%) hazardous waste sites that have had samples analyzed by the CLP (CLP 1988).

5.4.4 Other Media

Coal has been reported to contain silver at concentrations of up to 10 ppm (Boyle 1968). Klusek et al. (1983) measured the following silver concentrations at a bituminous coal-fired electric generating station: coal -- 0.29 mg/kg; fly ash -- 1.6 mg/kg; and bottom ash -- <0.1 mg/kg. In the combustible portions of municipal solid waste, mean silver concentrations were 3 ppm (range: <3-7 ppm) (Law and Gordon 1979). A municipal incinerator was found to emit particles containing 390 ppm silver (Law and Gordon 1979). The mean and maximum silver concentrations in U.S. sewage sludge were 225 mg/kg and 960 mg/kg (dry weight), respectively (Bunch 1982). Sludge silver concentrations (mg/kg dry weight) were reported as follows: from sewage treatment plants with industrial or municipal wastes -- 15-120 mg/kg; from plants with photoprocessing effluents as a source -- 450-27,000 mg/kg (Lytle 1984).

Scow et al. (1981) reported that the median silver concentrations in sewage treatment plant influent and effluent were 0.008 mg/L and 0.002 mg/L, respectively. Treated effluents from a large photographic processing plant contained an average of 0.07 mg/L silver (range: <0.02-0.30 mg/L) in the form of silver thiosulfate complexes, silver bromide, and silver sulfide (Bard et al. 1976).

Cunningham and Stroube (1987) collected samples of various foods in 20 U.S. cities between 1979 and 1980. Silver concentrations (mg/kg wet weight) in composite samples of the following food groups were: dairy products -- <0.061; meat, fish, and poultry -- mean 0.015, range 0-87; cereal and grain products -- mean 0.008, range 0-0.140; leafy vegetables -- mean 0.007, range 0-0.039; fruits -- <0.050; oils and fats -- <0.030. The average silver concentration of a mixture of 201 foods prepared to represent the typical U.S. diet was 0.0091 mg/kg dry weight (Iyengar et al. 1987). The average concentration in cow's milk in the United States has been reported to be 0.047 ppm (range: 0.037-0.059 ppm) (Murthy and Rhea 1968). EPA (1980a) summarized data on silver content in food as follows: beef -- 0.004-0.024 mg/kg; pork -- 0.007-0.012 mg/kg; mutton and lamb -- 0.006-0.011 mg/kg; tea -- 0.20-2.00 mg/kg (dry weight); mollusks -- 0.1-10.0 mg/kg.

Mean silver concentrations in one brand of nonfilter and filter cigarettes were reported to be 0.18 mg/kg and 0.27 mg/kg, respectively (Nadkarni et al. 1970).

In a summary of 1975-1979 data on fish tissue from EPA's STORET database, the mean concentration of silver in 221 samples was 0.225 mg/kg (wet weight

5. POTENTIAL FOR HUMAN EXPOSURE

total fish), with a range of 0.004-1.900 mg/kg (Scow et al. 1981). In Lake Pontchartrain, Louisiana (which is likely to receive substantial inputs of metals from municipal and agricultural activities) silver concentrations in clams and American oyster tissues were 0.4-2.4 mg/kg and 5.5 mg/kg (all dry weight), respectively (Byrne and DeLeon 1986)

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Food and water are the most likely major sources of exposure to natural and anthropogenic silver for the general U.S. population (Letkiewicz et al. 1984). The general population is also exposed through the inhalation of airborne silver and the dental and medical uses of silver. Letkiewicz et al. (1984) estimated that about 50% of the 214 million people in the United States who use public drinking water supplies had silver present in their water at 0.01-10 $\mu\text{g/L}$; 10-30% may receive water with levels greater than 30 $\mu\text{g/L}$. They estimated that 46,000 people in the U.S. receive drinking water with silver concentrations exceeding the current U.S. Safe Drinking Water Act maximum contaminant limit of 50 $\mu\text{g/L}$. Swimming pool water purified with silver-containing systems is another possible source of exposure to silver.

The averaged daily dietary intake (including fluids) of silver has been estimated to be 70 $\mu\text{g/day}$ (Snyder et al. 1975) and 88 $\mu\text{g/day}$ (Kehoe et al. 1940). The average daily dietary intake of two subjects over 30 days was determined to be 35-44 $\mu\text{g/day}$ (Tipton et al. 1966). The silver content of food was estimated at 4.5 $\mu\text{g/day}$ based on the content of a mixture of 201 foods prepared to represent the typical U.S. diet (Iyengar et al. 1987). Most of the U.S. population breathes air containing a maximum of 1.0 ng/m^3 silver, which contributes a maximum of 0.023 $\mu\text{g/day}$. Drinking water supplies containing 10 $\mu\text{g/L}$ would provide an estimated 20 $\mu\text{g/day}$ of the 70-88 $\mu\text{g/day}$ estimated daily intake. At levels of 30-50 $\mu\text{g/L}$, drinking water contributes 60-100 $\mu\text{g/day}$ (based on an estimated daily water intake of 2 L) and constitutes the major source of silver intake (Letkiewicz et al. 1984). Although silver has been detected in cigarettes, the average daily intake from smoking has not been determined. A very limited use of silver salts is in purification systems in isolated locations (such as mountain cabins and in space missions) (Silver Institute 1975).

The 1972-1974 National Occupational Hazard Survey (NOHS), conducted by NIOSH estimated that 19,343 workers in 2,163 plants were potentially exposed to silver in 1970 (NIOSH 1976). The largest number of exposed workers were in special trade contracting, primary metal industries, and industries using electrical machinery and electrical equipment and supplies. The occupational groups with the largest number of exposed workers were air conditioning, heating and refrigeration mechanics and repairmen; plumbers and pipefitters; miscellaneous assemblers; welders and flamecutters; and miscellaneous machine operators.

5. POTENTIAL FOR HUMAN EXPOSURE

Preliminary data from a second workplace survey, the 1980-1983 National Occupational Exposure Survey (NOES) conducted by NIOSH, indicated that 67,054 workers, including 15,763 women, in 3,123 plants were potentially exposed to silver in the workplace in 1980 (NIOSH 1984a). These estimates were derived from observations of the actual use of silver (67% of total estimate) and the use of trade name products known to contain the compound (33%). The largest number of workers were exposed in the primary metal industries, business services, health services, instruments and related products industries, and fabricated metal products industries.

Neither the NOHS nor the NOES databases 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.

Additional industrial processes which act as potential sources of occupational exposure to silver include the processing of silver chemicals such as silver nitrate and silver oxide for uses such as photography, and smelting and refining of silver-containing ores (DiVincenzo et al. 1985).

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

The most likely sources of higher than background levels of silver for the general population are ingestion of contaminated food and drinking water. The estimated 46,000 persons in the United States whose drinking water contains more than 50 $\mu\text{g/L}$ silver (attributable to natural and/or anthropogenic sources) would have an estimated daily intake of at least 100 $\mu\text{g/day}$ from water alone (Letkiewicz et al. 1984). Higher levels of silver have been detected in shellfish near industrial or sewage inputs (Byrne and DeLeon 1986; Pesch et al. 1977; Thomson et al. 1984) and are likely to occur in crops grown on sludge-amended soils, in the vicinity of smelters or mining operations, or in areas with naturally high background silver levels.

Elevated atmospheric silver concentrations have been attributed to smelting and refining of silver and other metals, and the use of silver iodide in cloud seeding (Scow et al. 1981). Populations living close to mines may have higher exposures. Approximately 71% of domestic mine production occurs in Idaho, Arizona, and Colorado; the Coeur d'Alene River Basin in Idaho supplies the greatest amount of silver (Drake 1980). Crops grown on soils with elevated silver concentrations (either from anthropogenic sources or from naturally high background levels) or exposed to high ambient atmospheric concentrations are likely to become enriched with silver (Ragaini et al. 1977; Ward et al, 1979).

Silver has been used in lozenges and chewing gums designed to aid the cessation of smoking. Silver acetate in chewing gum has been classified as an over-the-counter smoking deterrent by the Food and Drug Administration (Malcolm et al. 1986). Several cases of high body levels of silver have been

5. POTENTIAL FOR HUMAN EXPOSURE

reported (Malcolm et al. 1986). A skin silver concentration thousands of times higher than would be expected as a normal value was found in a patient after an estimated 6 month exposure to silver acetate lozenges (East et al. 1980; MacIntyre et al. 1978).

Scow et al. (1981) estimated that a person developing six rolls of film could be exposed to up to 16 grams of silver through dermal contact with photographic solutions. However, many people use implements or wear gloves during film developing and therefore this is not expected to result in widespread, high level exposures. Inhalation was not expected to be a significant route of uptake during film processing because of the low volatility of silver in solution.

5.7 ADEQUACY OF THE DATABASE

Section 104 (i) (5) of CERCLA, 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 silver 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 silver.

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 Identification of Data Needs

Physical and Chemical Properties. No data exist on the partition coefficients and Henry's law constant for silver and its compounds. A vapor pressure has been determined for silver at very high temperatures (greater than 900°C), but not for any of its compounds. Generally, the fate of silver in the environment is fairly well understood; however, a determination of these environmentally relevant values for silver compounds might provide a more complete estimation of the fate of silver in the environment. Tables 3-7 to 3-12 contain information on the known physical and chemical properties of silver and several important silver compounds.

Production, Use, Release, and Disposal. The production, use, release, and disposal of silver is well characterized and indicates that risk of exposure for the general population is potentially high. Silver and silver compounds are produced and used for a wide variety of common products and

5. POTENTIAL FOR HUMAN EXPOSURE

applications, including photographic materials, jewelry, tooth amalgams, medical supplies, and water purification. The extensive production and use of silver leads to a high risk of release to the environment, particularly to soil and water. Silver has been detected in various food products, with the highest levels detected in fish. Silver is both rare and valuable, and consumption exceeds production. Therefore, manufacturers attempt to conserve the metal by limiting releases and recycling instead of disposing of the metal. Methods exist for recovering silver from several waste media. Improvements in capturing released silver before it reaches the environment would be beneficial for both economic and health reasons.

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 EPA. The Toxics Release Inventory (TRI), which contains this information for 1987, became available in May of 1989. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. The factors governing the environmental fate of silver are not well characterized. While silver and its compounds are transported in the air, water, and soil, and are partitioned between these media, the mechanisms of transport and partitioning are not well-defined. No partition coefficients or constants have been determined for silver or its compounds. Little information was found in the available literature on transformation of silver in water or soil. Some microorganisms present in these media may be able to transform silver and silver compounds; however, silver is not expected to be significantly transformed in the environment because it is toxic to microorganisms. Further information on the size and flux of environmental compartments and the transport and transformations of silver and silver compounds in the environment would be useful in defining pathways for potential human exposure.

Bioavailability from Environmental Media. Silver is known to be absorbed from the lungs following inhalation exposure to silver dust or air contaminated with silver compounds, but data on the extent and rate of absorption are limited. Silver is also absorbed following oral or dermal exposure to drinking water, solutions and medical products containing silver compounds. No data were located on bioavailability of silver from soil, plant material, or foods. However, silver is found in all these environmental media and it is likely that some silver might be absorbed from these sources. Further information on the bioavailability of silver from contaminated air, water, soil, plants, and other foods would help in assessing the health risk associated with increased exposures that might occur in populations in the vicinity of hazardous waste sites.

Food Chain Bioaccumulation. The data available indicate that silver can bioconcentrate to a limited extent in algae, mussels, clams, and other aquatic

5. POTENTIAL FOR HUMAN EXPOSURE

Food Chain Bioaccumulation. The data available indicate that silver can bioconcentrate to a limited extent in algae, mussels, clams, and other aquatic organisms. However, many of the studies that were performed do not conform to the current state of the art in terms of sample size, duration, and analysis of contaminant levels in aquaria. Reliable data would be useful in determining the possibility of biomagnification and in defining pathways for general population exposure, as well as in estimating exposures from NPL site contamination.

Exposure Levels in Environmental Media. Silver has been detected in all environmental media, but most of the data are not current. Current data from EPA's CLP indicate silver is found at levels above background in ground water, surface water and soil near hazardous waste sites. Elevated levels of silver have been detected in shellfish located near sources of silver pollution. Estimates of average daily human intake from air, drinking water, food, and total diet have been calculated. More current information, that better defines major sources and forms of silver, would increase the accuracy of estimates of daily exposure to silver. This information could be used to develop a more thorough representation of the contribution of silver exposure from contamination at hazardous waste sites. Data that better characterize levels in fish and shellfish would aid in identifying populations with potentially high exposures to silver from these sources.

Exposure Levels in Humans. Silver has been detected in the blood, tissues, urine, and feces of humans. The only biological monitoring studies located consisted of small numbers of worker populations in chemical manufacturing industries. Studies that better characterize important sources of general population exposure and define populations with potentially high exposure, such as those located near hazardous waste sites, would be helpful. More specific information concerning the chemical form of silver present at hazardous waste sites would also be useful. These data would assist in developing a more accurate estimate of the potential for silver exposure from hazardous waste sites contaminated with the metal.

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

5.7.2 On-going Studies

No long-term research studies on the environmental fate of silver were identified. However, environmental monitoring being conducted in conjunction with remedial investigation/feasibility studies at NPL sites where silver has

5. POTENTIAL FOR HUMAN EXPOSURE

been found should add useful information regarding environmental concentrations, chemical species, fate, and transport of the compounds.

No on-going studies or long-term research concerning occupational or general population exposures to silver were identified.

