

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Thallium is a heavy metallic element that exists in the environment mainly combined with other elements (primarily oxygen, sulfur, and the halogens) in inorganic compounds. Thallium is quite stable in the environment, since it is neither transformed nor biodegraded.

Compounds of thallium are generally soluble in water and the element is found primarily as the monovalent ion (Tl^+). Thallium tends to be sorbed to soils and sediments (Frantz and Carlson 1987; Mathis and Kevern 1975; Wallwork-Barber et al. 1985) and to bioconcentrate in aquatic plants, invertebrates, and fish (Barrows et al. 1978; Zitko and Carson 1975). Terrestrial plants can also absorb thallium from soil (Ewers 1988; Sharma et al. 1986).

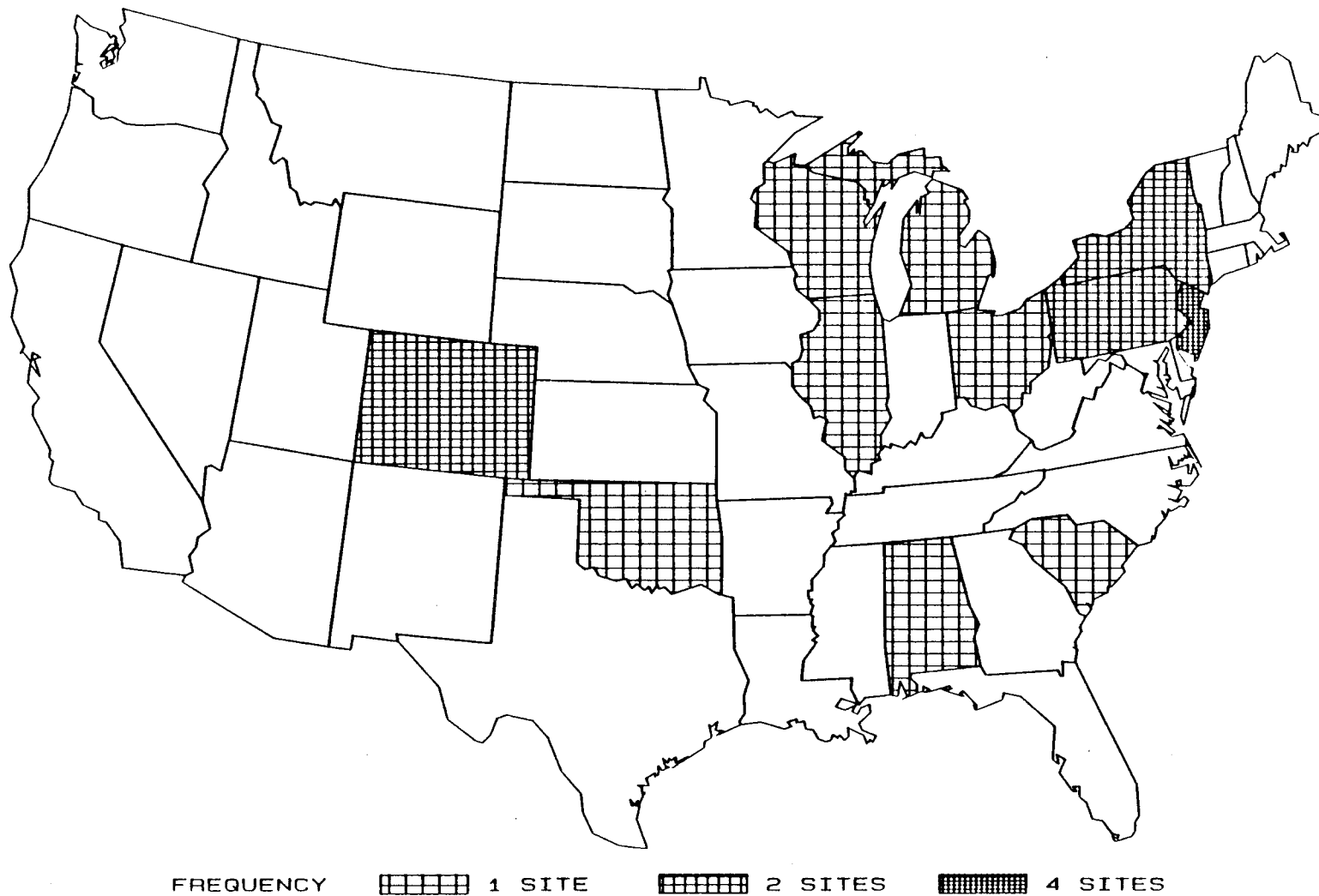
Major releases of thallium to the environment are from processes such as coal-burning and smelting, in which thallium is a trace contaminant of the raw materials, rather than from facilities producing or using thallium compounds. Humans may be exposed to thallium by ingestion, inhalation, or dermal absorption. However, the general population is exposed most frequently by ingestion of thallium-containing foods, especially home-grown fruits and green vegetables. Inhalation of contaminated air near emission sources or in the workplace may also contribute to thallium exposure of some individuals.

The EPA has identified 1,177 NPL sites. Thallium has been found at 18 of the sites evaluated for this chemical. However, we do not know how many of the 1,177 sites have been evaluated for this chemical. As more sites are evaluated, these numbers may change (View 1989). The frequency of these sites within the United States can be seen in Figure 5-1. Seventeen sites are located in the United States and 1 site is located in the commonwealth of Puerto Rico (not shown).

5.2 RELEASES TO THE ENVIRONMENT

Manufacturers, processors, and users of thallium and thallium compounds are required to report quantities of releases of these substances to environmental media annually (EPA 1988c). According to the SARA Section 313 Toxics Release Inventory (TRI), an estimated total of 56,511 pounds of thallium were released to the environment from manufacturing and processing facilities in the United States in 1987 (Table 5-1) (TRI 1989). The TRI data should be used with caution since the 1987 data represent first-time reporting by these facilities. Only certain types of facilities were required to report. This is not an exhaustive list. However, the major sources of

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



* Derived from View 1989

TABLE 5-1. Releases to the Environment from Facilities
That Manufacture or Process Thallium and Compounds^a

Facility	Location	Total (lbs)						Off-site transfer
		Air	Underground injection	Water	Land	Environment	POTW ^b transfer	
Philips Industries, Inc., Dexter Axle Div	Albion, IN	54,411	0	0	0	54,411	0	39,639
Tenneco Oil Company	Chalmette, LA	0	No Data	0	0	0	No Data	3
Koch Refining Company	Saint Paul, MN	0	0	1,100	0	1,100	No Data	0
River Cement Company	Festus, MO	250	0	0	0	250	0	0
Sohio Oil Company Toledo Refinery	Oregon, OH	0	0	750	0	750	0	0
Dana Corporation	Reading, PA	No Data	No Data	No Data	0	No Data	0	250
Totals		54,661	0	1850	0	56511	0	39892

^aDerived from TRI 1989

^bPOTW -- publicly-owned treatment works

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thallium releases to the environment are not from facilities that produce or use thallium and its compounds, but from processes such as coal-burning or smelting in which thallium is a trace element of the raw materials (Schoer 1984). Data on thallium emissions from these sources are not included in the TRI.

5.2.1 Air

Thallium is released to the atmosphere mainly from coal-burning power plants, cement factories, and ferrous and nonferrous smelting operations (EPA 1988a; Ewers 1988; Sharma et al. 1986). Thallium emissions in the United States were estimated at 140 tons/year each from coal-burning power plants and from iron and steel production (Ewers 1988; Schoer 1984; Smith and Carson 1977). Total air releases reported from industrial sources were about 27 tons in 1987 (TRI 1989).

Davison et al. (1974) reported concentrations of thallium on airborne fly ash emitted from a coal-burning power plant ranging from 29 to 76 $\mu\text{g/g}$, the thallium concentration increasing with decreasing particle size. The highest concentrations (greater than 60 $\mu\text{g/g}$) were on particles less than 7.3 μm in diameter. The authors reported that these concentrations were representative of eight other United States power plants burning various types of coal. The highest thallium concentrations were also found on the smaller diameter (0.2 - 0.8 μm) particles of fly dust emitted from a West German cement plant (Ewers 1988).

No quantitative estimates of thallium emissions from other domestic sources were located. However, additional sources of airborne thallium may include manufacturers of alloys, artificial gems, electronics equipment, optical glass, and domestic heating plants (EPA 1987a; Sharma et al. 1986; Valerio et al. 1988).

5.2.2 Water

The major sources of thallium releases to water include nonferrous metals, iron and steel manufacturers and various mining, inorganic chemicals, refining, and ore-processing industries (EPA 1980a, 1983c; Ewers 1988). Thallium concentrations in raw or treated waste waters from these industries ranged up to 2 g/L (EPA 1983c). Thallium has been detected in urban waste waters, apparently from commercial and industrial sources (Callahan et al. 1979a; Levins et al. 1979). Total water releases reported from industrial sources were 1,850 pounds in 1987 (TRI 1989). Thallium has been detected in both surface and groundwater samples at hazardous waste sites. Data from the Contract Laboratory Program (CLP) Statistical Database indicate that thallium occurred in surface water at 1% of sites at a geometric mean concentration of 23 ppb in positive samples and in groundwater at 7% of sites at a mean concentration of 11 ppb in positive samples (CLPSD 1989). Note that the Contract Laboratory Program (CLP) Statistical Database includes data from both

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NPL and non-NPL sites. No other quantitative estimates of total thallium releases to water were located.

5.2.3 Soil

Thallium releases to soil are mainly solid wastes from coal combustion and smelting operations (Ewers 1988). Thallium was detected at a geometric mean concentration of 1.7 ppm in positive soil samples from 3.5% of an unspecified number of hazardous waste sites (CLPSD 1989). Although direct soil releases are likely to be small, since thallium-containing wastes are subject to EPA land disposal restrictions, atmospheric thallium pollution may contribute to soil contamination in the vicinity of thallium emission sources (Brockhaus et al. 1981). It should be noted that land disposal restrictions were implemented by EPA in 1987. Prior to this time disposal of pesticides had been to municipal and industrial landfills. Since thallium is relatively stable in the environment, we can assume that landfills, as well other Superfund sites, contain thallium or thallium-containing products.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Thallium is a nonvolatile heavy metal, and if released to the atmosphere by anthropogenic sources, may exist as an oxide (thallium oxide), hydroxide (TlOH), sulfate (thallium sulfate), or as the sulfide Tl_2S (EPA 1988a). These thallium compounds are not volatile (EPA 1983c; Weast 1970). It has been speculated that thallium sulfate and TlOH will partition into water vapor (such as clouds and rain drops) because they are soluble in water and thus, precipitation may remove these forms of thallium from the atmosphere (EPA 1988a). Thallium oxides are less soluble in water, and may be subject to only atmospheric dispersion, and gravitational settling. No corroborative information was located. The atmospheric half-life of suspended thallium particles is unknown.

Thallium exists in water primarily as a monovalent ion (thallium⁺); thallium may be trivalent (Tl^{3+}) in very oxidizing water (Callahan et al. 1979b). Tl^+ forms complexes in solution with halogens, oxygen, and sulfur (Lee 1971). Thallium may precipitate from water as solid mineral phases. However, thallium chloride, sulfate, carbonate, bromide, and hydroxide are very soluble in water. For example, the solubility of thallium sulfate at 0°C is about 27 g/L (EPA 1980a). In extremely reducing water, thallium may precipitate as a sulfide (Tl_2S), and in oxidizing water, Tl^{3+} may be removed from solution by the formation of $Tl(OH)_3$ (Lee 1971). Stephenson and Lester (1987a, 1987b) argued that the partial removal of thallium from water was the result of precipitation of unknown solids during the treatment of sewage sludge.

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Thallium may partition from water to soils and sediments. Mathis and Kevern (1975) presented indirect evidence that thallium was adsorbed by lake sediments. Furthermore, thallium may be adsorbed by micaceous clays in solution (Frantz and Carlson 1987).

Partition coefficients such as adsorption constants describe the tendency of a chemical to partition to solid phases from water. Adsorption constants for inorganic ions such as Tl⁺ cannot be predicted a priori, but must be measured for each adsorbent. Thallium adsorption data in Magorian et al. (1974) for a hectorite clay (a rare montmorillonite clay mineral) at pH 8.1 suggest that an adsorption constant for this specific system may be approximately 19 L/g. No other information on the adsorption of thallium by earth materials was located.

Thallium may be bioconcentrated by organisms from water. A bioconcentration factor (BCF) relates the concentration of a chemical in the tissues of aquatic animals or plants to the concentration of the chemical in the water in which they live. Experimentally-measured BCF values have been reported: 18.2 for clams and 11.7 for mussels (Zitko and Carson 1975). Bioconcentration factors for the muscle tissue of juvenile Atlantic salmon have ranged from 27 to 1,430 (Zitko et al. 1975). The maximum BCF for bluegill sunfish was 34 in the study of Barrows et al. (1978). Thallium is absorbed by plants from soil and thereby enters the terrestrial food chain (Ewers 1988; Sharma et al. 1986). Cataldo and Wildung (1983) demonstrated that thallium could be absorbed by the roots of higher plants from the rhizosphere.

5.3.2 Transformation and Degradation

5.3.2.1 Air

Metallic thallium oxidizes slowly in air (Lee 1971), and thallos chloride is photosensitive (Cotton and Wilkinson 1980). However, there was no evidence that thallium is transformed significantly by photochemical reactions in the atmosphere (Callahan et al. 1979b).

5.3.2.2 Water

Little is known about thallium transformation in water by either abiotic or biotic processes (EPA 1988a). Pertinent data regarding the photolysis or hydrolysis of common thallium compounds were not located.

5.3.2.3 Soil

Callahan et al. (1979b) concluded that there was no evidence that thallium is biotransformed in the environment. No other information was located.

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5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT**5.4.1 Air**

Data on thallium levels in ambient air are sparse. In six United States cities, the thallium concentrations ranged from 0.02 to 0.1 ng/m³, with a typical concentration of 0.04 ng/m³ (EPA 1980a, 1988a). Concentrations of thallium in Chadron, Nebraska reportedly ranged from 0.04 to 0.48 ng/m³ (EPA 1980a, 1988a), and geometric mean concentrations measured during 1985-1986 in Genoa, Italy were about 0.015 µg/m³ (Valerio et al. 1988). The estimated thallium concentration near a coal-burning power plant was 0.7 µg/m³ (EPA 1988a).

Thallium levels have also been measured in workplace air. Marcus (1985) reported maximum thallium levels in workplace air at 0.014 and 0.022 mg/m³ during machining and alloying operations, respectively, of a magnesium alloy used in batteries at a plant in England. Air samples in two cement plants and two foundries in Italy had thallium concentrations of less than 1 µg /m³ (Apostoli et al. 1988).

5.4.2 Water

Since thallium is a naturally-occurring element, it may be present in ambient waters in trace amounts. However, monitoring data indicate elevated thallium concentrations near industrial and commercial sources and hazardous waste sites.

A survey of tap water from 3,834 homes in the United States detected thallium in 0.68% of samples at an average thallium concentration of 0.89 µg/L (EPA 1980a, 1988a). Thallium was detected in 10% of urban stormwater runoff samples at concentrations ranging from 1 to 14 µg/L (Cole et al. 1984). Thallium has been measured in seawater at 0.01-14.00 µg/L (Sharma et al. 1986).

Water concentrations of thallium in rivers in the United States and Canada that receive mining operations effluents ranged from 0.7 to 88.3 µg/L (EPA 1980a, 1988a; Zitko et al. 1975).

5.4.3 Soil

Estimates of thallium concentration in the earth's crust range from 0.3 to 0.7 ppm (EPA 1988a), so thallium is likely to be present in soils in trace amounts. The limited data available indicate that soil thallium levels may be increased near thallium-emitting industrial sources and at hazardous waste sites. Measured thallium concentrations in lake sediments ranged from 0.13 to 0.27 µg/g in four remote Rocky Mountain lakes (Heit et al. 1984) to 2.1-23.1 mg/kg (mean value 13.1 mg/kg) in a Michigan lake reportedly polluted by airborne particulate matter (EPA 1988a). Up to 5 mg/kg thallium was

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reported in stream sediments near metal industry runoff areas (Wallwork-Barber et al. 1985).

5.4.4 Other Environmental Media

Trace amounts of thallium are found in most foods (Ewers 1988), but few foods, except vegetables grown in thallium-polluted soil, are likely to have significant thallium concentrations (Ewers 1988; Sharma et al. 1986).

Data on thallium content of specific foods grown and consumed in the United States were not located. However, a recent study of the thallium content of food in the United Kingdom reports levels of thallium in meat, fish, fats, and green vegetables (Sherlock and Smart 1986).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Human exposure to thallium may occur by inhalation, ingestion, or dermal absorption. The general population is exposed most frequently by ingestion of thallium-containing foods (EPA 1980a, 1988a; Ewers 1988). From the very limited data available, EPA estimated daily intakes for the general adult population from drinking water, air, and food (EPA 1980a). More recent data on thallium concentrations in food and dietary intake of the general population (Sherlock and Smart 1986) confirm that food (green vegetables in particular) is probably the major source of thallium exposure. Although these data are from the United Kingdom, it is not likely that the thallium content of the food supply of the United States would be significantly different. Limited data on thallium concentrations in cigars and cigarettes suggest smoking may be a source of thallium. The extent of exposure from this source is not clear since thallium levels in cigarette smoke are not known. Table 5-2 summarizes the estimated typical daily intakes from water, food, and air.

Occupational exposure to thallium may be significant for workers in smelters, power plants, cement factories, and other industries that produce or use thallium compounds or alloys. Exposure may occur by dermal absorption from handling thallium-containing compounds, ores, limestone, or cement or by inhalation of workplace air (Ewers 1988; Marcus 1985; Schaller et al. 1980).

Urinary thallium levels are considered the most reliable indicator of thallium exposure. Although data on exposure levels in workplace air are rare (see Section 5.4.1), studies associating workplace exposure and elevated urinary thallium confirm the occurrence of industrial exposures in Europe (Apostoli et al. 1988; Marcus 1985; Schaller et al. 1980). Similar data were not located for U.S. workplaces. However, NIOSH estimated that more than

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TABLE 5-2. Summary of Typical Human Exposure to Thallium^a

Parameter	Exposure medium		
	Water	Air	Food
Typical concentration in medium	0.89 $\mu\text{g/L}$	0.48 ng/m^3	ND-50 $\mu\text{g/kg}$
Assumed intake of medium by 70-kg adult	2 L/day	20 m^3/day	1.5 kg
Assumed absorption fraction	1.0	0.35	1.0
Estimated daily intake by 70-kg adult	$\approx 2 \mu\text{g}$	3.4 ng	5 μg

^aAdapted from EPA 1980a, 1988a; Sherlock and Smart 1986

ND = not detected

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1,600 people are occupationally exposed to thallium in the United States (NOES 1989). The NOES database does not contain information on the frequency, concentration, or duration of exposure of workers to any of the chemicals listed therein. This survey provides only estimates of the number of workers potentially exposed to chemicals in the workplace.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Populations with potentially high exposures are those living near coal-burning power plants, metal smelters, or cement plants (Sharma et al. 1986). The airborne particulate emissions from these plants may have high thallium levels, especially on the small-diameter, respirable particles (Davison et al. 1974; Ewers 1988). Human populations living in the vicinity of these plants may be exposed by inhalation or by ingestion of fruits and vegetables homegrown in contaminated soils (Brockhaus et al. 1980, 1981; EPA 1988a; Sharma et al. 1986).

Workers in industries producing or using thallium-containing materials also have potentially high exposures as noted above (Section 5.5).

Limited data suggest that smokers may have potentially high exposure to thallium. Although recent authoritative evaluations of cigarette smoke constituents do not include thallium, thallium was detected at 0.057-0.170 $\mu\text{g/g}$ in cigar stubs and 0.024 $\mu\text{g/g}$ in cigarette tobacco (EPA 1980a; Smith and Carson 1977). One study indicates that the urinary excretion of thallium in smokers is about twice that of nonsmokers (EPA 1980a; Smith and Carson 1977).

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 thallium is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of thallium.

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.

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5.7.1 Data Needs

Physical and Chemical Properties. Additional measurements of the aqueous solubility of environmentally relevant thallium compounds would provide a more accurate basis for applying mineral equilibria to predict the fate of thallium in water (EPA 1988a).

Production, Import/Export, Use, and Disposal. According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the 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.

Data on production, use, and disposal (HSDB 1989; TRI 1989; U.S. Bureau of Mines 1988) are adequate. Additional information is unlikely to significantly affect estimates of human exposure.

Environmental Fate. Little information is available on partitioning of thallium in the atmosphere (EPA 1988a). This lack of data is not important since thallium is nonvolatile. The reaction mechanisms controlling the fate of thallium in water are not well known. Adsorption-desorption reactions with soils and sediments (Frantz and Carlson 1987; Magorian et al. 1974; Mathis and Kevern 1975) suggest that movement of thallium can be reduced. Additional research would provide a more accurate basis for predicting the fate of thallium in water. Very little is known about potential transformation mechanisms for thallium in air, water, or soil (Callahan et al. 1979b; EPA 1988a), but this lack of detailed data may not be a major limitation because many transition metals are not susceptible to transformation or degradation-type processes.

Bioavailability From Environmental Media. Thallium can be absorbed following inhalation of contaminated workplace air, ingestion of contaminated food, or dermal contact (Dai-xing and Ding-nan 1985; Dolgner et al. 1983; Marcus 1985). The most significant routes of exposure near hazardous waste sites are likely to be through drinking thallium-contaminated water and skin contact with or ingestion of thallium that is attached to soil particles. Information on the percent of thallium taken into the body from environmental media that is actually absorbed or bioavailable would be useful in clarifying the toxic potential of thallium in humans. The relative absorption of different species/forms of thallium from inorganic and biological matrices would also be useful.

Food Chain Bioaccumulation. There are no specific data on the bioaccumulation of thallium or its potential to be transferred from lower trophic levels to higher organisms. Because thallium can be bioconcentrated, it may be that it can also be accumulated in living tissues. We know that

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thallium may be bioconcentrated by aquatic plants, invertebrates, and fish (Barrows et al. 1978; Zitko and Carson 1975; Zitko et al. 1975). Information on biotransformation in aquatic biota would provide further insight into the extent of chemical speciation and forms of thallium to which humans could be exposed near hazardous waste sites. Terrestrial plants absorb thallium from soil (Cataldo and Wildung 1983). Additional measurements of the bioconcentration of thallium by plants and animals and information on soil types and conditions which enhance thallium uptake by plants would be helpful to better define the tendency of thallium to partition to living tissues. Detectable levels of thallium have been found in many foods (Ewers 1988; Sharma et al. 1986; Sherlock and Smart 1986). However, no data were located on biomagnification of thallium in the food chain. Information on food chain bioaccumulation would be useful in assessing the potential for human exposure to thallium from food.

Exposure Levels in Environmental Media. Data on thallium levels in all environmental media are sparse (EPA 1988a). More research using sensitive analytical methods for all media, especially in the vicinity of potential thallium pollution sources and waste sites, and specific data on the thallium content of the American diet would increase the accuracy of human exposure estimates.

Exposure Levels in Humans. Thallium has been detected in human urine and urinary thallium excretion is used as a measure of thallium absorption (Dai-xing and Ding-nan 1985; Dolgher et al. 1983; Marcus 1985). Reliable data on urinary thallium in unexposed individuals and correlating urinary thallium levels with environmental exposures at hazardous waste sites would help to identify populations at risk in the vicinity of these sites from thallium exposure.

Exposure Registries. No exposure registries for thallium 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

Remedial investigations and feasibility studies conducted at the 18 NPL sites known to be contaminated with thallium will add to the available database on exposure levels in environmental media, exposure levels in humans, and exposure registries.

No other information was located on any on-going studies on the fate, transport, or potential for human exposure for thallium.