6. POTENTIAL FOR HUMAN EXPOSURE

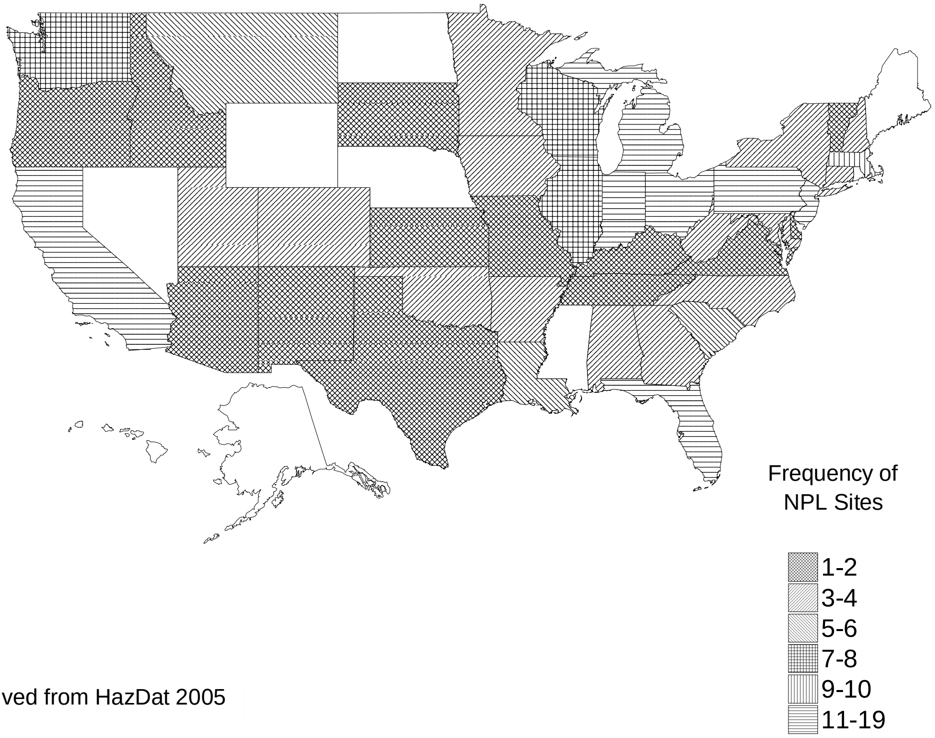
6.1 OVERVIEW

Tin and organotin compounds have been identified in at least 214 and 8 sites, respectively, of the 1,662 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2004). However, the number of sites evaluated for tin and organotin compounds is not known. The frequency of these sites can be seen in Figures 6-1 and 6-2, respectively. All sites where tin and organotin compounds were found are located in the United States.

Tin occurs naturally in the earth's crust with a concentration of approximately 2–3 ppm (Budavari 2001). Tin compounds are found in various environmental media in both inorganic and organic forms. Tin may be released to the environment from natural and anthropogenic sources. Tin is a component of many soils and inorganic tin compounds may be released in dusts from wind storms, roads, and agricultural activities. Releases of tin to environmental media may occur from the production and use of tin and tin compounds. Gases, dusts, and fumes containing tin may be released from smelting and refining processes, industrial uses of tin, waste incineration, and burning of fossil fuels (Byrd and Andreae 1986; Senesi et al. 1999; WHO 1980). In general, organotin compounds are released to the environment from anthropogenic sources; however, methyltin compounds can be produced in the environment by biomethylation of inorganic tin and can occur naturally (Fent 1996). Antifouling paints containing tributyltin are applied as a finish coat to the immersed sections of boats and floating structures. As the paint releases tributyltin into the water, it creates an environment that repels the organisms that may attach to the surface of submerged objects. Use of antifouling paints represents the major source of tributyltin into the coastal environment (Alzieu 1998). The use of tributyltin compounds as slimicides on masonry, disinfectants, and biocides for cooling systems, power station cooling towers, pulp and paper mills, breweries, leather processing, and textile mills (WHO 1990) may result in their release to the environment. Triphenyltin enters the environment directly from its use as a pesticide. To a lesser extent, organotin compounds may also enter the environment by leaching to soil and groundwater from consumer products containing organotin compounds disposed of in landfills (Fent 1996).

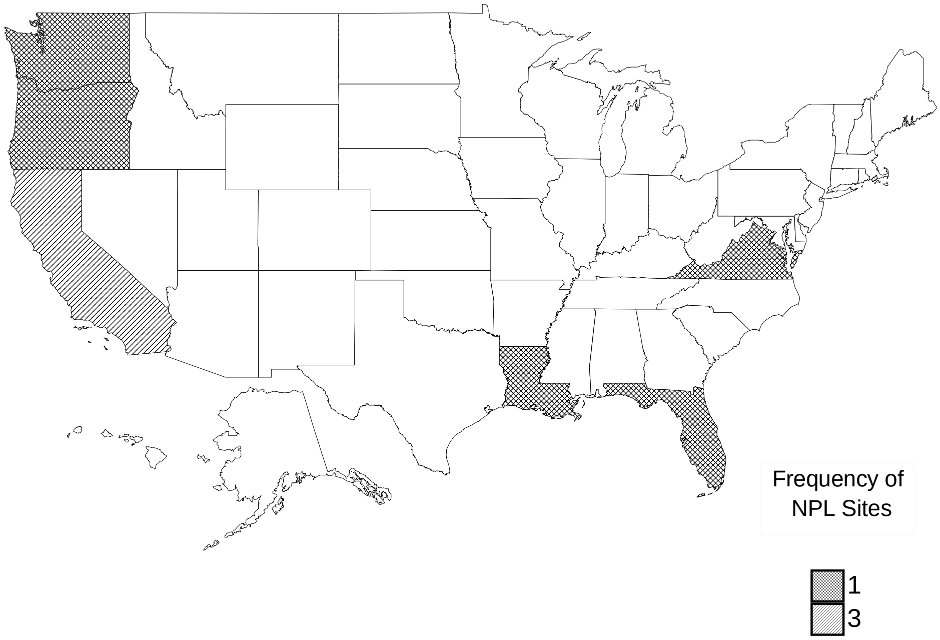
Tin may exist in either divalent (Sn^{2+}) or tetravalent (Sn^{4+}) cationic (positively charged) ions at environmental conditions. Tin(II) dominates in reduced (oxygen-poor) water, and will readily precipitate as a sulfide (SnS) or as a hydroxide ($Sn(OH)_2$) in alkaline water. Tin(IV) readily hydrolyzes, and can precipitate as a hydroxide. In general, tin(IV) would be expected to be the only stable ionic species in the

Figure 6-1. Frequency of NPL Sites with Tin Contamination



Derived from HazDat 2005

Figure 6-2. Frequency of NPL Sites with Organotin Contamination



Derived from HazDat 2005

weathering cycle (Wedepohl et al. 1978). Tin in water may partition to soils and sediments. Cations such as Sn^{2+} and Sn^{4+} will generally be adsorbed by soils to some extent, which reduces their mobility. Tin is generally regarded as being relatively immobile in the environment (Gerritse et al. 1982; WHO 1980).

Organotin compounds are generally only sparingly soluble in water and are likely to partition to soils and sediments. Most commercially used organotin compounds are relatively immobile in environmental media due to their low vapor pressures, low water solubilities, and high affinities for soil and organic sediments (Blunden et al. 1984). For example, nearly all of the tributyltin found in the water column is bound to suspended particles, with a small portion associated with dissolved organic matter and organic and inorganic ligands (Gadd 2000). Tributyltin that is associated with particles in the water column may settle out, which is an important process in its removal from the water column. Tributyltin sorption coefficients to sediments can range from 100 to 10,000 (Anderson et al. 2002). Degradation of organotin compounds involves breaking the tin-carbon bond and can occur in the environment by ultraviolet (UV) irradiation, or biological or chemical cleavage (Blunden et al. 1984). Rates of photodegradation and biodegradation of organotins in water are dependent upon environmental conditions. In sediment, organotins are generally persistent. Organotin compounds may be significantly bioconcentrated by aquatic organisms. Cleavage of the tin-carbon bond by hydrolysis is not a significant environmental fate process under environmental conditions (WHO 1990).

Occupational exposure to tin may be significant in some industrial environments. Ambient environmental levels of tin are generally quite low, except in the vicinity of pollution sources. Humans may be exposed to tin by inhalation, ingestion, or dermal absorption. However, typical human exposure to tin is primarily by ingestion of food. Tin-lined cans used to package food constitute the most important contribution to tin intake in the diet (Biégo et al. 1999). While there is evidence that tin is essential for the normal growth of rats, there is no evidence that tin is essential for other animals, including humans (WHO 1980). Exposure to organotin compounds may occur by the ingestion of seafood and contact with consumer products that contain organotin compounds. Household commodities made up of polyurethane, plastic polymers, and silicons contain butyltin concentrations in the parts per million range (Kannan et al. 1999). Mono- and dimethyltin and mono- and dibutyltin compounds have been detected in drinking water in Canada where polyvinyl chloride (PVC) pipes, containing these organotin compounds, are used in the distribution of drinking water (Sadiki and Williams 1996, 1999; Sadiki et al. 1996). Organotin compounds were detected in household dust in the United Kingdom (Santillo et al. 2003).

6.2 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 1997). Manufacturing and processing facilities are required to report information to the TRI only if they employ 10 or more full-time employees; if their facility is classified under Standard Industrial Classification (SIC) codes 20–39; and if their facility produces, imports, or processes ≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 1997).

There is no information on releases of tin and tin compounds from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997). However, releases of tin to environmental media may occur from the production and use of tin and tin compounds.

Tin and organotin compounds have been identified in a variety of environmental media (air, surface water, leachate, groundwater, soil, and sediment) collected at 214 and 8 sites, respectively, of the 1,662 current or former NPL hazardous waste sites (HazDat 2004).

6.2.1 Air

There is no information on releases of tin and tin compounds to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997).

Tin has been identified in air collected at 6 of the 214 current or former NPL hazardous waste sites where it was detected in some environmental media. No organotin compounds were found in air at the eight current or former NPL hazardous waste sites where organotin compounds were detected in some environmental media (HazDat 2004).

Tin may be released to the atmosphere from both natural and anthropogenic sources. Tin is a component of many soils and may be released in dusts from wind storms, roads, and agricultural activities. Gases, dusts, and fumes containing tin may be released from smelting and refining processes, industrial uses of tin, waste incineration, and burning of fossil fuels (Byrd and Andreae 1986; Senesi et al. 1999; WHO 1980). Davison et al. (1974) reported that the tin content of airborne fly ash from coal-burning power plants ranged from 7 to 19 μg/g. Worldwide emissions of tin to the atmosphere from coal and oil combustion, refuse incineration, and copper/nickel production facilities were estimated at 1,470–

10,810 metric tons in 1983 (Nriagu and Pacyna 1988). Organotin compounds may be released to air by agricultural spraying, volatilization, antifouling paint sprays, incineration of materials treated or stabilized with organotin compounds, and glass coating operations. Incineration of organotin containing material is unlikely to be a significant source of organotin compounds to air, since these compounds will be decomposed to inorganic tin during combustion (Blunden et al. 1984). Releases of organotin compounds to air are not significant due to their low vapor pressures and rapid photodegradation (Blunden et al. 1984; Fent 1996).

6.2.2 Water

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

Tin has been identified in groundwater and surface water at 78 and 36 sites, respectively, of the 214 NPL hazardous waste sites where it was detected in some environmental media. Organotin compounds were found in surface water at one of the eight current or former NPL hazardous waste sites where they were detected in some environmental media; organotin compounds were not found in groundwater at these sites (HazDat 2004).

Releases of tin to water may occur from industrial facilities smelting, refining, or using tin (WHO 1980). Antifouling paints containing tributyltin are applied as a finish coat to the immersed sections of boats and floating structures. As the paint releases tributyltin into the water, it creates an environment that repels the organisms that may attach to the surface of submerged objects. Use of antifouling paints represents the major source of tributyltin into the coastal environment. It has been estimated that one boat releases 1–10 μg tributyltin/cm^2 of hull surface daily to ensure antifouling protection. This corresponds to 0.2–2 g/day for a small sailboat and up to 50–500 g/day for an average sized merchant ship (Alzieu 1998). The use of triorganotin compounds as marine antifoulants has been restricted by the Organotin Antifouling Paints Control Act (June 16, 1988), which limits the type of vessel on which these paints can be used, and limits the use of tributyltin paints that have laboratory tested release rates of ≤ 4 μg/cm^2/day (Cardwell et al. 1999a). Most industrialized countries, in addition to the United States, have adopted similar restrictions on the use of tributyltin containing paints. These countries include the United Kingdom, Canada, France, New Zealand, Australia, and the European Union (Birchenough et al. 2002).

Organotin compounds may also be released to water from overspray and land runoff from agricultural applications, industrial processes, and leaching from organotin-stabilized polyvinyl chloride (PVC) (Blunden et al. 1984). The use of tributyltin compounds as slimicides on masonry, disinfectants, and biocides for cooling systems, power station cooling towers, pulp and paper mills, breweries, leather processing, and textile mills may result in their release to the environment (WHO 1990). Triphenyltin acetate and triphenyltin hydroxide are used as fungicides, algicides, and molluscicides (WHO 1999). Timber treatment facilities can be as a significant source of tributyltin in freshwater systems from seepage, accidental spills, and intentional releases. Minor sources of organotin compounds in freshwater can be seepage from landfill sites and agricultural runoff, due to the use of contaminated sewage sludge or organotin containing pesticides (Demora and Pelletier 1997). Monthly samples of influent, effluent, and sludges were collected from July 1990 to January 1991 from sewage treatment plants in five Canadian cities. Monobutyltin was detected in all influent samples. Dibutyl- and tributyltin were only detected infrequently, and octyltin species were not detected. A significant reduction, 40% on average, in the concentration of monomethyltin was found after passage through the sewage treatment plants, due to degradation and adsorption to sludge. No butyltin or octyltin species were found in five landfill leachate samples in southern Ontario, Canada (Chau et al. 1992).

6.2.3 Soil

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

Tin has been identified in soil at 121 sites and in sediment at 49 sites collected from 214 NPL hazardous waste sites, where it was detected in some environmental media. Organotin compounds were found in sediment and soil at four sites and one site, respectively, of the eight current or former NPL hazardous waste sites where they were detected in some environmental media (HazDat 2004).

Tin may be released to soil from organotin pesticide usage and landfilling of tin-containing wastes, including used cans and organotin-containing plastics (WHO 1980). The application of pre-treated municipal sludge and urban refuse as soil amendments may also introduce tin to soils. Concentrations of tin in sewage sludges from countries in Europe and North America ranged from 40 to 700 mg/kg dry weight. Manures and poultry wastes contained tin at concentrations of 3.7–7.4 and 2.0–4.1 mg/kg dry weight, respectively. Other incidental point sources that may introduce tin to soil are corrosion of metal objects and dispersion of metallic ores during transport (Senesi et al. 1999). Organotin compounds may be released to soil through agricultural applications and burial of organotin-containing waste material (Blunden et al. 1984). An estimated 5,200 tons of organotin compounds were released, primarily to landfills in the United States in 1976 (Laughlin and Linden 1985). No current data were found regarding releases of organotin compounds to soil.

6.3 ENVIRONMENTAL FATE

6.3.1 Transport and Partitioning

Tin may be transported in the atmosphere by the release of particulate matter derived from the combustion of fossil fuels and solid wastes. The vapor pressure of elemental tin is negligible (Cooper and Stranks 1966), and inorganic tin compounds are nonvolatile at environmental conditions. Airborne particles may travel long distances before deposition depending on the type of emitting source, physical form and properties (e.g., size, density), physical or chemical changes that may occur during transport, adsorption processes, and meteorological conditions (Senesi et al. 1999).

Tin may exist in either divalent (Sn^{2+}) or tetravalent (Sn^{4+}) cationic (positively charged) ions at environmental conditions. Tin(II) dominates in reduced (oxygen-poor) water, and will readily precipitate as a sulfide (SnS) or as a hydroxide ($Sn(OH)_2$) in alkaline water. Tin(IV) readily hydrolyzes, and can precipitate as a hydroxide. The solubility product of $Sn(OH)_4$ has been measured at approximately 10^{-56} g/L at 25 °C. In general, tin(IV) would be expected to be the only stable ionic species in the weathering cycle (Wedepohl et al. 1978).

Tin in water may partition to soils and sediments. Cations such as Sn^{2+} and Sn^{4+} will generally be adsorbed by soils to some extent, which reduces their mobility. Tin is generally regarded as being relatively immobile in the environment (Gerritse et al. 1982; WHO 1980). However, tin may be transported in water if it partitions to suspended sediments (Cooney 1988), but the significance of this mechanism has not been studied in detail. Transfer coefficients for tin in a soil-plant system were reported to be 0.01–0.1 (Senesi et al. 1999).

A bioconcentration factor (BCF) relates the concentration of a chemical in plants and animals to the concentration of the chemical in the medium in which they live. It was estimated that the BCFs of inorganic tin were 100, 1,000, and 3,000 for marine and freshwater plants, invertebrates, and fish, respectively (Thompson et al. 1972). Marine algae can bioconcentrate tin(IV) ion by a factor of 1,900 (Seidel et al. 1980).

Approximately 95% of tributyltin in the water column was found to be bound to suspended particles and the remainder was associated with dissolved organic matter and organic and inorganic ligands (Gadd 2000). Tributyltin that is associated with particles in the water column may settle out, which is an important process in the removal of tributyltin from the water column. Tributyltin sorption coefficients to sediments can range from 100 to 10,000 (Anderson et al. 2002). A partition coefficient of about 2,180 at 20 °C was calculated by Maguire et al. (1985) to estimate the adsorption of tributyltin ions by lake sediments. These investigations also concluded that the half-life of the desorption reaction was about 10 months, indicating that tributyltin can be strongly retained by sediments. The adsorption behavior of Sn^{4+} ion and eight organotin species (tri-, di-, and monobutyltin; tri-, di-, and monomethyltin; and tri- and diphenyltin) were studied in a water-sediment system using artificial seawater and estuarine sediment. Adsorption coefficients varied from $10^{0.5}$ to $10^{4.5}$ and showed the trend of Sn^{4+} > mono > di > tri in the same substituent series. Larger absorption coefficients were found for aromatic compounds than for aliphatic compounds (Sun et al. 1996). Sediment-water partition coefficients for tributyltin ranged from 240 to 65,000 in sediments of the coast of southwestern Spain. Similar values were found for monobutyltin. Dibutyltin was found to have higher affinity for sediment (Gomez-Ariza et al. 2001).

At ambient temperatures, the solubilities of organotin compounds range from 0.0001 to about 50 mg/L (Laughlin and Linden 1985; WHO 1980). Organotin compounds may partition from water to aquatic organisms. An octanol/water partition coefficient (K_{ow}) describes the partitioning of an organic chemical between octanol and water. Octanol is believed to best imitate the fatty structures in plant and animal tissues (Kenaga and Goring 1980). The K_{ow} of tributyltin at pH 6 was reported to be about 1,585 by Maguire et al. (1983). The most accurate K_{ow} for tributyltin in seawater was 5,500 (Laughlin and Linden 1985).

There is no evidence of biomagnification of tributyltin in marine ecosystems, but accumulation may occur, resulting in high tissue concentrations in some organisms (Meador 2000). Rüdel (2003) reported that, based on a review of the literature, the bioavailability of organotin compounds via the food chain appears to be of minor importance for tributyltin and triphenyltin when compared to uptake via the water phase. Measured BCF values for bis(tributyltin)oxide with marine oysters were found to range from 2,300 to 11,400 (Waldock and Thain 1983). A BCF of 30,000 was estimated by Maguire et al. (1984) for the bioconcentration of tributyltin cation by freshwater green algae. Seven-day BCF values were derived for dibutyltin dichloride, dibutyltin dilaurate, tributyltin chloride, bis(tributyltin) oxide, and triphenyltin chloride for muscle, liver, kidney, and vertebra tissue of round crucian carp. The BCF values ranged from 12 in muscle to 5,012 in liver. For all organotin compounds, liver had the highest BCF values. The highest BCFs were found for the tributyltin compounds (Tsuda et al. 1986). BCF values for bis(tributyltin) oxide for red sea bream (*Pagrus major*), mullet (*Mugil cephalus*), and filefish (*Rudarius erodes*) were 9,400–11,000, 2,400–3,000, and 3,200–3,600, respectively, determined in an 8-week flow-through aquarium system. Larger BCF values were obtained when fish were reared in seawater containing lower concentrations of tributyltin. BCF values for triphenyltin chloride for *P. major* and *R. erodes* were 3,100–3,300 and 4,100, respectively, and were independent of the concentration of triphenyltin in the rearing water (Yamada and Takayanagi 1992). The log BCFs for tributyltin in fish from the Port of Osaka and the Yodo River, Japan were 3.6–4.2 and 2.9–3.5, respectively (Harino et al. 2000). After 50 days of exposure to water containing a constant concentration of tributyltin (500 ng/L), whole body concentrations in tilapia did not reach a plateau, and the 50-day BCF was 12,300. Enrichment of tributyltin was highest in the viscera, followed by gill, and then muscle (Hongxia et al. 1998). A BCF of 10,500 was found for tributyltin uptake from seawater in marine mussels (*Mugil graynus*) during the 56-day accumulation phase (Suzuki et al. 1998). BCFs were 17,000–350,000, 2,000–70,000, and 1,000–70,000 for tri-, di-, and monobutylin, respectively, in mollusks living in southwest Spain, showing a decrease in BCF with decreasing lipophilicity for the butyltin compounds (Gomez-Ariza et al. 2001).

Bioconcentration as a function of pH was studied for triphenyltin and tributyltin in a freshwater sediment organism, *Chironomus ripaius*. At pH 5 and 8, respectively, the BCFs were 310 and 170 for tributyltin, and 680 and 510 for triphenyltin. While the difference in BCF at the two pHs was statistically significant for tributyltin, it was not for triphenyltin. This may be explained by the speciation differences for each of these compounds as pH varies. The acid dissociation constant (pK_a) of tributyltin is 6.25, and at pH 5, the fraction of tributyltin hydroxide is approximately 5%, with the tributyltin cation as the predominant species in solution. The pK_a for triphenyltin is 5.2, and at pH 5, approximately 40% is present as triphenyltin hydroxide with the remainder as triphenyltin cation. The differences in the observed pH dependence between triphenyltin and tributyltin may indicate that the neutral hydroxide species is the predominant form taken up by the organism. BCF values of 1,500 and 1,200 at pH 5 and 8, respectively, were determined for tetrabutyltin ion, which cannot undergo ionization and was used as a control compound. The difference between these BCF values for tetrabutyltin at pH 5 and 8 was not statistically significant (Looser et al. 1998).

Releases of organotin compounds to air from various surfaces are, in general, not significant due to their low vapor pressures and rapid photodegradation at surfaces (Fent 1996). It has been reported that methylation of inorganic and organotin compounds, such as di- and tributyltin, are likely to occur in sediments, producing potentially volatile organotin compounds. This process may lead to mobilization of tin species into the water column and possibly into the atmosphere. However, there is currently no significant evidence of losses of organotin compounds to the atmosphere (Amouroux et al. 2000). There was no indication that tributyltin in water partitioned to the air during a 62-day period, whereas 20% of the water evaporated (Maguire et al. 1983).

6.3.2 Transformation and Degradation

6.3.2.1 Air

No information was located on the transformation or degradation of tin compounds in the atmosphere.

6.3.2.2 Water

Inorganic tin cannot be degraded in the environment, but may undergo oxidation-reduction, ligand exchange, and precipitation reactions (HSDB 2003). It has been established that inorganic tin can be transformed into organometallic forms by microbial methylation (Hallas et al. 1982). Inorganic tin may also be converted to stannane (H_4Sn) in extremely anaerobic (oxygen-poor) conditions by macroalgae (Donard and Weber 1988).

The speciation of organotin compounds is pH-dependent. At lower pHs, the cationic form will be the primary form, and as the pH is increased, the neutral hydroxide compounds will be the predominant species. In the environmentally relevant pH range (pH 5–9), the predominant organotin species will be the neutral hydroxide compounds (i.e., R_3SnOH, $R_2Sn(OH)_2$, and $RSn(OH)_3$). High concentrations of chloride favor the formation of chloro species. The pK_a values for trimethyltin, triethyltin, tributyltin, and triphenyltin cations are approximately 6.60, 6.81, 6.25, and 5.2, respectively (Blunden et al. 1984; Fent 1996; Meador 2000).

Degradation of organotin compounds involves the breaking of the tin-carbon bond, which may occur by UV irradiation, or by biological or chemical cleavage (Blunden et al. 1984). In water, tributyltin can be degraded by photochemical and biological processes relatively rapidly; however, adsorption onto suspended particulate material in water followed by sedimentation is a key removal process (De Mora and Pelletier 1997). The half-life of tributyltin in seawater varies, depending on pH, temperature, turbidity, and light; it is generally estimated to be in the range of 1 day to a few weeks (Alzieu 1998). Biodegradation is the major process in seawaters rich in suspended solids, but photolysis, in surface waters, exceeds biodegradation in clean seawater. Calculated half-lives range from 6 days in summer-time waters rich in suspended particles to 127 days in clean winter waters (Watanabe et al. 1992). Tributyltin can be degraded by microbial, microalgal, and fungal populations, as well as by some higher organisms, such as fish (Anderson et al. 2002). Cleavage of the tin-carbon bond by hydrolysis is not an important fate process under environmental conditions (WHO 1990).

6.3.2.3 Sediment and Soil

Inorganic tin cannot be degraded in the environment, but may undergo oxidation-reduction, ligand exchange, and precipitation reactions (HSDB 2003). Degradation of organotin compounds in sediments is much slower than in water, and half-lives have been estimated to be several years (Alzieu 1998). In addition to dealkylation of organotin compounds, methylation of tin and organotin compounds by chemical and/or biological means may occur. The contribution of methylation by biotic and abiotic mechanisms is not clear. This pathway may result in fully substituted and volatile tin compounds. Methylated butyltin compounds, such as tributylmethyltin and dibutyldimethyltin, have been found in contaminated harbor sediments and in surface waters (Amouroux et al. 2000; Cooney 1988). Methylation of tin in sediments was found to be positively correlated with increasing organic content in sediment and to follow predominately a biotic pathway (Hadjispyrou et al. 1998).

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to tin and tin compounds depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of tin and tin compounds in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on tin and tin compounds levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable. The analytical methods available for monitoring tin and tin compounds in a variety of environmental media are detailed in Chapter 7.

Environmental monitoring studies may report concentrations of organotin compounds in various environmental media in two formats, either as mass of tin per unit mass or volume of media, or as mass of organotin ion per unit mass or volume of media. To convert mass on a tin basis to mass on an organotin cation basis, multiply by the ratio of the formula weight of the organotin cation to the atomic weight of tin. Conversions are provided in Table 6-1 for various organotin cations. For example, a tributyltin (TBT) concentration in sediment reported as 122 ng TBT/g would correspond to 50 ng Sn/g, since tributyltin ion has a mass that is 2.44 times greater than that of tin.

6.4.1 Air

Tin is detected in air infrequently and at low concentrations, except in the vicinity of industrial sources. Air concentrations in U.S. cities ranged from below the detection limit to 0.8 μg/m^3 in several studies. Average concentrations are generally <0.1 μg/m^3, with higher concentrations near some industrial facilities (EPA 1982a; WHO 1980). In some studies, tin was not detected in 40–>50% of samples. Atmospheric tin is associated with particulate matter, and peak concentrations were found on smaller respirable particles (1–3 μm) (WHO 1980). Samples of airborne inhalable particulate matter were collected in two urban/industrial areas in Illinois, southeast Chicago and East St. Louis, over a 2-year period. Average tin concentrations in the fine (<2.5 μm) and coarse (2.5–10 μm) particulate fractions were <0.007 and 0.012 μg /m^3 for East St. Louis, respectively, and <0.007 μg /m^3 for both the fine and course fractions in samples from southeast Chicago and a rural site in Bondville, Illinois (Sweet and Vermette 1993). The average tin concentration in highway tunnel exhaust aerosol in the Elbtunnel in Hamburg, Germany between August 1988 and January 1989 was 10.9 μg/m^3 (Dannecker et al. 1990). Tin concentrations in the particulate matter in the ambient air at art glass manufacturing plants measured by personal samples from oven-charger and batch-mixer workers ranged from 0.1 to 3.5 μg/m^3 from three plants that use arsenic as a fining agent (a fining agent is added to disperse air bubbles in glass). Tin was not detected in the particulate matter in the air at three other plants that use antimony compounds instead of arsenic (Apostoli et al. 1998). No monitoring data for concentrations of organotin compounds in air were found.

6.4.2 Water

Tin occurs in trace amounts in natural waters. However, it is seldom measured and only infrequently detected, since concentrations are often below the detection limit (NAS 1977; WHO 1980). In surface waters, tin was detected in only 3 of 59 samples from 15 U.S. and Canadian rivers at concentrations ranging from 1.3 to 2.1 μg/L, and not detected in 119 samples from 28 U.S. rivers. A mean tin concentration of 0.038 μg/L was reported for surface water in Maine (NAS 1977; WHO 1980). Tin

Table 6-1. Conversion Between Mass on a Tin Basis to Mass on an Organotin Cation Basis

To convert from mass on a tin basis:	To:	Multiple by:
	mass on a TBT cation basis	2.44
	mass on a DBT cation basis	1.96
	mass on a MBT cation basis	1.48
	mass on a TMT cation basis	1.38
	mass on a DMT cation basis	1.25
	mass on a MMT cation basis	1.13
	mass on a TPT cation basis	2.95
	mass on a DPT cation basis	2.30
	mass on a MPT cation basis	1.65

DBT = dibutyltin; DMT = dimethyltin; DPT = diphenyltin; MBT = monobutyltin; MMT = monomethyltin; MPT = monophenyltin TBT = tributyltin; TMT = trimethyltin; TPT = triphenyltin concentrations in public water supplies ranged from 1.1 to 2.2 μg/L in 42 U.S. cities and from 0.8 to 30 μg/L in 32 of 175 water supplies in Arizona (NAS 1977; WHO 1980). Tin concentrations in drinking water have been reported at <10 μg/L (WHO 2003). Tin is present in seawater at about 0.2–3 μg/L (NAS 1977; WHO 1980). Tin concentration in fresh snow from the French Alps collected in 1998 at different altitudes ranged from 157 to 436 pg/g (Veysseyre et al. 2001).

Concentrations of tributyltin (TBT) were found to range from 20 to 1,800 ng TBT/L in the Chesapeake Bay area, Maryland (Hall 1988). In surface waters from San Diego Bay, California in 1986–1989, tributyltin levels averaged 4.7–13 ng TBT/L in the north bay, 1.3–9.9 ng TBT/L in the south bay, 3.5–14 ng TBT/L in U.S. Navy pier regions, and 19–120 ng TBT/L in yacht harbors. Tributyltin concentrations in bottom waters in the San Diego Bay area ranged from 8.8 to 61 ng TBT/L. The mean tributyltin concentrations in regional surface waters from Pearl Harbor, Hawaii from 1986 to 1989 were: 0.0–6.8 ng TBT/L in channels; 0.0–4.9 ng TBT/L in outlying regions; 2.4–31 ng TBT/L in Southeast Loch; and 6.7–130 ng TBT/L in a small marina. Tributyltin concentrations in bottom waters in Pearl Harbor ranged from 0.0 to 9.7 ng TBT/L. In Honolulu harbor, surface and bottom water tributyltin concentrations were 4.8–580 and 2.6–170 ng TBT/L, respectively (Grovhoug et al. 1996). Tributyltin concentrations in surface water from the harbor area of Osaka City, Japan ranged from 2 to 33 ng TBT/L (Harino et al. 1998). Butyltin compounds were detected in 32 of the 63 seawater samples (0.5 m depth) that were collected from 18 areas along the Japanese coast from 1997 to 1999. Average butyltin concentrations were 4.6 ng MBT/L, 4.5 ng DBT/L, and 6.8 ng TBT/L from sampling stations for each of the four areas: the Pacific coast of northern Japan, the coast along the Sea of Japan, Tokyo Bay and the adjacent area, and western Japan. The highest concentrations in these four areas were found in western Japan with concentrations of 5.9 ng MBT/L, 6.9 ng DBT/L, and 20.1 ng TBT/L (Takeuchi et al. 2004).

The seasonal variations in tributyltin concentrations in marinas on Lake Ontario were studied from April to December 1998. The marinas were at Toronto, Mississauga, Oakville, Hamilton, and Fifty Point, Canada. Approximately 150–200 pleasure boats were in each marina in the summer. Tributyltin concentrations increased with increased boat activity, with a maximum concentration of 14 ng Sn/L reported in late August at Fifty Point. Concentrations of tributyltin varied at the marinas, peaking between June and September, but were always higher in the marinas compared to a reference site, Burlington, Canada, that was far from any marinas (Yang and Maguire 2000). Similar seasonal variations were seen in seawater collected from marinas and harbors from southwestern Spain. Tri-, di-, and monobutyltin concentrations were significantly higher in water collected in May and August compared to water collected in November and February. The highest concentrations were found in waters in enclosed areas with poor water turnover. Tributyltin concentrations ranged from <0.5 to 31 ng Sn/L. Analysis for phenyltin compounds was performed, but none were found (Gomez-Ariza et al. 2001).

While many studies reported on the occurrence of organotin compounds in marine environments fewer studies reported the occurrence of organotin compounds in freshwater. A study investigating the levels of di- and tributyltin in fresh surface waters from nine sites across the United States found that, at most sites, di- and tributyltin were not detected (detection limits were 970 and 180 ng butyltin ion/L for dibutyltin and tributyltin, respectively). The highest dibutyltin concentrations were found in water sampled in 1998 from the Neuse River, North Carolina and Contentnea Creek, North Carolina at 140 and 160 ng DBT/L, respectively. Tributyltin was only detected in the Little Missouri River, North Dakota and Flat River, North Carolina at concentrations of 265 and 600 ng TBT/L, respectively (Jones-Lepp et al. 2004). Bancon-Montigny et al. (2004) reported a monitoring study involving sampling along 11 rivers in southwest France from February to October 2001. Sites were chosen to represent specific industrial or agricultural activities. Organotin compounds were detected in most water samples; butyltin compounds were most frequently detected with concentrations generally ranging from below the detection limit (0.2 ng Sn/L) to 30 ng Sn/L. Phenyltin compounds were also detected at concentrations generally ranging from below the detection limit (0.2 ng Sn/L) to 20 ng Sn/L. High phenyltin concentrations were detected during the spring and the end of the summer and likely are derived from agricultural sources. Monophenyltin concentrations from over 400 up to 700 ng Sn/L were detected at four sampling sites. Octyltin compounds were detected as well; however, concentrations were generally lower, ranging from below the detection limit (0.2 ng Sn/L) to 15 ng Sn/L (Bancon-Montigny et al. 2004).

Mono- and dimethyltin and mono- and dibutyltin compounds have been detected in Canadian drinking water. Drinking water in Canada is distributed through PVC pipes stabilized with methyl- and butyltin compounds. Methyl- and butyltin compounds were detected at concentrations up to 22 and 43.6 ng Sn/L, respectively, in distributed water samples from six municipalities in Canada (Sadiki and Williams 1996). Tap water in 10 of 22 homes collected in February 1995 from five Canadian municipalities contained monomethyltin and dimethyltin compounds at concentrations of 0.5–257 and 0.5–6.5 ng Sn/L, respectively. No organotin compounds were detected in the tap water from the other 12 houses. No organotin compounds were detected in raw water or in water just after leaving the treatment plant, suggesting that the source of these organotin compounds was from some component of the distribution system (Sadiki et al. 1996). Canadian drinking water samples collected during the winter–spring 1996 from 28 sites and autumn 1996 from 21 sites were found to contain monomethyltin, dimethyltin, monobutyltin, and dibutyltin in ranges of <0.5–290.6, <0.5–49.1, <0.5–28.5, and <0.5–52.3 ng Sn/L, respectively. These compounds were detected with a frequency of 84, 80, 16, and 12% in the winter–spring survey and 100, 57, 7, and 7% in the autumn survey, respectively. A summer 1996 survey of locations with the highest organotin concentrations in the winter–spring survey showed a decrease in mono- and dimethyltin concentration in 89% of the samples. This finding was consistent with laboratory studies that showed organotin release from PVC into water decreases after a few days. PVC pipe/tubing contains organotin compounds consistent with the organotin patterns found in the distributed water samples. Octyltin compounds, which are not used as stabilizers in the PVC used to distribute drinking water, were not detected in drinking water samples. Octyltin compounds are used instead as heat stabilizers in PVC for food packaging. Except for one treated water sample, no organotin compounds were detected in raw or treated water collected at the water treatment plant or in distributed water supplied through polyethylene pipes (Sadiki and Williams 1999).

Organotin compounds were measured in precipitation and fog in the forested catchment in Northeast Bavaria, Germany during 2001–2002. Mono-, di-, and tri methyl and butyl derivatives, as well as mono- and dioctyltin compounds were detected in precipitation samples collected in this study. The median total organotin concentrations in bulk precipitation, throughfall, and fog were 5.83, 14.6, and 57.1 ng Sn/L, respectively, over the year-long monitoring study. Monoalkyl tin compounds were the dominant species found in precipitation, with concentrations up to 192 ng Sn/L for monobutyltin in fog (Huang et al. 2004).

6.4.3 Sediment and Soil

Tin concentrations in soil are generally low, except in areas where tin containing minerals are present (Bulten and Meinema 1991). Tin concentrations in the earth's crust are approximately 2–3 mg/kg (Budavari 2001). Tin concentrations in soil can range from 2 to 200 mg/kg, but in areas of high tin deposits, levels of 1,000 mg/kg may occur (Schafer and Fembert 1984; WHO 1980). The mean background soil concentration in the United States is 0.89 mg/kg (Eckel and Langley 1988). Tin concentrations in topsoil (0–7.6 cm) from the western end of East St. Louis, Illinois ranged from <13 to 1,130 mg/kg. East St. Louis has a history of industrial facilities including smelters of ferrous and nonferrous metals, a coal-fired power plant, chemical producing companies, and petroleum refineries (Kaminski and Landsberger 2000a). Sediment cores collected in January 1996 from Central Park Lake in New York City, New York contained average tin concentrations ranging from 4.0 mg/kg at 44–47 cm depth to 67 mg/kg at 22–24 cm depth. The average tin concentration in surface sediments (0–2 cm depth) in Central Park Lake was 32 mg/kg. The similarities between the history of municipal solid waste incineration in New York City and the accumulation of trace metals in the Central Park Lake sediments appear to be consistent with incineration being the major source of several metals to the New York City atmosphere (Chillrud et al. 1999). Tin concentrations in sediments from the Wah Chang Ditch and the northeast corner of Swan Lake, an area that received runoff from a Texas tin smelter during the 1940s and 1950s, were found to be as high as 8,000 mg/kg (Park and Presley 1997).

Organotin concentrations in sediment are summarized in Table 6-2. While tributyltin concentrations in water have declined since restrictions on tributyltin use in paints have been in place, concentrations of tributyltin in sediments have remained relatively high. Degradation of tributyltin in sediment is much slower than in the water column. Recent surveys of tributyltin concentrations in harbors and marinas in various countries show concentrations ranging from hundreds of parts per billion (μg/kg) to low parts per million (mg/kg) (Meador 2000). Tributyltin concentrations in sediment samples from the harbor area of Osaka City, Japan ranged from 0.002 to 0.966 mg TBT/kg dry weight (Harino et al. 1998). Sediment in southwestern Spain during November 1993–February 1994 and May–August 1994 were analyzed for the presence of butyl- and phenyltin compounds. No phenyltin species were found in sediment, but mono-, di-, and tributyltin were found at all stations sampled, with concentrations of tributyltin ranging from <0.0006 to 0.16 mg Sn/kg dry weight. Increased concentrations of organotin concentration during summer months were not observed in the sediment, as they were in water and biota, and may be due to vertical mixing of the sediment layers by natural and boating activities (Gomez-Ariza et al. 2001). Tri-, di-, and monobutyltin were detected in superficial sediment samples from five river estuaries (Deba, Urola, Oria, Oiartzun, and Bidasoa) of Gipuzkoa, North Spain at concentrations of 0.05–5.48, 0.15–0.71, and 0.86–2.87 mg Sn/kg dry weight, respectively. Except for one sampling point, monobutyltin, a degradation product of tributyltin, accounted for the largest percentage of total butyltin (>47%) (Arambarri et al. 2003). Sediments collected in November 1997 from three sites near Nuuk, Greenland contained tributyltin concentrations ranging from <0.001 to 0.171 mg Sn/kg dry weight (Jacobsen and Asmund 2000). Tributyltin concentrations were measured in sediment collected in 1997 and 1999 from transects along and perpendicular to the shipping lanes in the Sound (Øresund) and the Kattegat/Skagerrak region, an important shipping strait between Denmark and Sweden. Tributyltin concentrations ranged from 0.0015 to 0.0188 mg TBT/kg dry weight in the Sound and were below the detection limit (<0.001 mg TBT/kg dry weight) in the Kattegat region. A strong correlation was observed between tributyltin concentration and the organic fraction in sediment samples from the Sound (Strand et al. 2003).

Bancon-Montigny et al. (2004) reported a monitoring study involving sampling along 11 rivers in southwest France from February to October 2001. Sites were chosen to represent specific industrial or

Table 6-2. Organotin Levels in Sediment

Nature/location of sediment	Concentration of organotin compound				Units	Reported as	Reference
Central-west Greenland, near Nuuk Harbor, surface sediment							
	TBT	DBT	MBT		mg Sn/kg dw	Mean	
Sandkaj	0.0097	0.0039	<0.001				Jacobsen and Asmund 2000
Havnen	0.171	0.0096	<0.001				
Hundeøen	<0.001	<0.001	<0.001				
St. Lawrence River in the Quebec City area, surface sediments							
	TBT	DBT	MBT	DPT	mg Sn/kg dw	Mean	Regoli et al. 2001
Portneuf	0.097	0.286	0.989	<0.001			
Sillery	0.146	0.165	0.087	<0.001			
Quai Lévis	0.173	0.496	0.123	0.015			
Bassin Louise	0.888	0.997	0.203	<0.001			
Outside Bassin Louise	0.807	0.634	0.185	<0.001			
St. Charles River	0.330	0.579	0.165	<0.001			
St. Lawrence Marina	0.209	0.389	0.004	0.101			
Île d'Orléans East	0.211	0.045	0.006	<0.001			
Superficial sediments from five river estuaries (Deba, Urola, Oria, Oiatzun, and Bidasoa) of Gipuzkoa, North Spain, October 2000							
	TBT	DBT	MBT		mg Sn/kg dw	Range	Arambarri et al. 2003
	0.05–5.48	0.15–0.71	0.86–2.87				
Huelva coast, southwest Spain							
(November 1993–February 1994)	TBT	DBT	MBT		mg Sn/kg dw	Average	Gomez-Ariza et al. 2001
Canela	0.0067	0.017	0.0032				
Pinillos	0.0009	0.0026	0.0015				
Carreras River	0.0140	0.080	0.015				
Idla Cristana harbor	0.090	0.090	0.035				
Cantil marina	0.100	0.270	0.080				
Punta Caiman	0.0028	0.0037	0.0012				
Isla Cristina breakwater (inner part)	<0.0006	<0.0007	0.0034				
Terron harbor	28.0	46.0	45.0				
Palo	2.0	3.6	8.0				
Rompido marina	130.0	40.0	24.0				
Pino	0.8	0.7	0.9				
Punta Umbria harbor	16.0	69.0	13.0				

Table 6-2. Organotin Levels in Sediment

Nature/location of sediment	Concentration of organotin compound			Units	Reported as	Reference
Six sites from the lowermost Tennessee River and Kentucky Lake, United States, surface sediments (0–5 cm)						
	MBT	DBT	TBT	mg/kg dw[a]	Range	Loganathan et al. 1999
	<0.003–0.320	<0.001–0.014	0.0053–0.356			
Thirteen sites in the Sound (Øresund) between Denmark and Sweden, surface sediments, 1997						
	NR	NR	0.0015–0.0188	mg/kg dw[a]	Range	Strand et al. 2003
Twenty-four sites from Coddington Cove, Newport, Rhode Island, United States, surface sediments (0–2 cm), 1993 and 1994						
	NR	NR	0.032–0.372	mg Sn/kg dw	Range	Wade et al. 2004
Eighteen sites from 11 rivers in southwest France, surface sediments, July 2001						
	0.016–0.125	0.001–0.087	0.0013–0.089	mg Sn/kg dw	Range	Bancon-Montigny et al. 2004
Eighteen sites from 11 rivers in southwest France, surface sediments, September 2001						
	0.001–0.048	ND–0.037	ND–0.020	mg Sn/kg dw	Range	Bancon-Montigny et al. 2004

[a] Concentration reported as mg butyltin ion/kg sediment.

DBT = dibutyltin; DPT = diphenyltin; dw = dry weight; MBT = monobutyltin; ND = not detected; NR = no data reported; SD = standard deviation; TBT = tributyltin; TPT = triphenyltin agricultural activities. Mono-, di-, and tributyltin were present in nearly all surface sediment samples with concentrations ranging from 0.001 to 0.125, not detected to 0.087, and not detected to 0.089 mg Sn/kg dry weight, respectively. Mono-, di-, and triphenyltin and mono-, di-, and trioctyltin were also detected in some sediment samples, but with less frequency and generally at lower concentrations than the butyltin compounds (Bancon-Montigny et al. 2004).

Tri-, di-, and monobutyltin were detected in all sediment samples collected in the Quebec City harbor area of the St. Lawrence River with concentrations of 0.097–0.888, 0.045–0.997, and 0.004–0.989 mg Sn/kg dry weight, respectively. Diphenyltin was detected in two sites at concentrations of 0.015 and 0.101 mg Sn/kg dry weight. The organotin contamination found in this study was more comparable to levels reported for Canadian marine harbor sites than to freshwater harbor sites (Regoli et al. 2001). Tributyltin and dibutyltin concentrations in surface sediments (0–2 cm) collected in 1990 and 1992 from intertidal sites in Portland and Boothbay Harbor, Maine ranged from 0.024 to 12.4 mg TBT/kg and from 0.015 to 2.23 mg DBT/kg dry weight (Page et al. 1996). Tributyltin was detected in all 24 surface sediment (0–20 cm) samples collected from Coddington Cove, Newport, Rhode Island on November 3, 1993 and June 13, 1994; concentrations ranged from 0.032 to 0.372 mg Sn/kg dry weight with a mean concentration of 0.146 mg Sn/kg dry weight. Sediment cores of varying depth (up to 18 cm) were obtained from seven stations. Tributyltin was detected in all of these samples and ranged from 0.0073 to 0.225 mg Sn/kg dry weight. No consistent trends were observed in the tributyltin concentrations with depth, suggesting that mixing is an important process in the sediment column (Wade et al. 2004). Kentucky Lake constitutes the northernmost end of a shipping route for large barges and small ships between the Gulf of Mexico and the Ohio River. The lowermost Tennessee River receives industrial waste water from several industries in the Calvert City Industrial Complex. Total butyltin (BT) concentrations in the sediments of the lowermost Tennessee River and Kentucky Lake ranged from 0.0068 to 0.356 mg BT/kg dry weight (Loganathan et al. 1999).

6.4.4 Other Environmental Media

Tin and tributyltin concentrations found in foods are summarized in Tables 6-3 and 6-4, respectively. Tin concentrations of vegetables, fruits and fruit juices, nuts, dairy products, meat, fish, poultry, eggs, beverages, and other foods not packaged in metal cans are generally <2 mg/kg. Tin concentrations in pastas and breads have been reported to range from <0.003 to 0.03 mg/kg. Mean tin concentrations ranging from <1 to 1,000 mg/kg have been found in foods packaged in unlacquered or partially lacquered cans, while the average tin concentration in foods in lacquered cans has been reported to be 0–6.9 mg/kg

Table 6-3. Tin Levels in Food[a]

Food item	Concentration (mg/kg)	Reported as
Dietary intake in a French adult		
Preserved foods in unlacquered cans		
Tomatoes (n=3)	84 (46–156)	Mean, range
Artichoke (n=1)	106	
Mushrooms (n=3)	34 (24–45)	
Pineapples (n=5)	82 (44–136)	
Fruit cocktail (n=2)	97 (88–107)	
Peaches (n=3)	44 (27–71)	
Pears (n=2)	47 (35–60)	
Apricot (n=1)	114	
Stewed fruit (n=1)	30	
Grapefruit (n=1)	128	
Preserved foods in lacquered cans		
Bean (n=1)	2.4	Mean, range
Tomatoes (n=2)	6.0 (3.2–8.8)	
Asparagus (n=2)	3.9 (1.4–6.5)	
Garden peas (n=1)	1.0	
Mushrooms (n=2)	6.9 (0.4–13.4)	
Apricot (n=1)	5.8	
Cherry (n=1)	0.5	
Strawberry (n=1)	0.6	
Papaya (n=1)	2.9	
Meats (n=4)	4.5 (1.1–9.4)	
Fishes (n=4)	0.7 (0.3–0.9)	
Fresh foods		
Carrots (n=4)	0.08 (0.07–0.09)	Mean, range
Cabbage (n=1)	0.06	
Endive (n=1)	0.1	
Spinach (n=4)	<0.003	
Bean (n=1)	0.05	
Leek (n=1)	0.03	
Potatoes (n=5)	0.1 (0.1–0.2)	
Salad (n=4)	0.02 (0.01–0.03)	
Tomatoes (n=4)	0.05 (0.04–0.06)	
Lentils (n=2)	0.13 (0.09–0.17)	
Bananas (n=3)	<0.003	
Oranges (n=3)	0.07 (0.06–0.08)	
Pears (n=3)	0.07 (0.06–0.08)	
Apples (n=4)	0.04 (0.02–0.07)	
Apricots (n=2)	0.07 (0.06–0.08)	
Alcoholic beverages (n=10)	<0.003	

Table 6-3. Tin Levels in Food[a]

Food item	Concentration (mg/kg)	Reported as
Mineral waters (n=5)	<0.003	
Nonalcoholic beverages (n=10)	0.04 (<0.003–0.13)	
Fishes and crustaceans (n=10)	<0.003	
Breads (n=6)	<0.003	
Pasta (n=12)	<0.003	
Meats (n=15)	<0.003	
Cooked pork meats (n=10)	<0.003	
Milk (n=10)	<0.003	
Dairy products (n=10)	<0.003	
Sugar (n=5)	<0.003	
Chocolate (n=1)	<0.003	
Oil (n=4)	<0.003	

[a] Source: Biego et al. 1999

Table 6-4. Tributyltin (TBT) Levels in Food

Food item	Concentration (ng TBT/g) wet weight
Seafood from eight markets worldwide[a]	*Reported as mean*
Ulsan, Korea	
Mussel, soft tissue	115
Shrimp, whole body	33
Squid, muscle	23
Shrimp, tail only	19
Chub mackerel, muscle	12
Flounder, muscle	9.4
Marseille, France	
European squid, muscle	655
European squid, common cuttlefish, elegant cuttlefish, muscle	376
Mediterranean mussel, soft tissue	87
Red tuna, muscle	56
Common cuttlefish, muscle	14
Elegant cuttlefish, muscle	13
Green crab, muscle	3.6
Lemon sole, Senegalse sole, muscle	Not detected
Galveston, Texas, United States	
Pacific oyster, American oyster, soft tissue	72
Squid, muscle	16
Shrimp, whole body	12
Shrimp, tail only	11
Southern flounder, tropical flounder, muscle	6
Oyster, soft tissue	4.6
Blue runners, Atlantic bonito, muscle	4.5
Singapore	
Mackerel, muscle	23
Bigeye tuna, muscle	20
Mitre squid, muscle	12
Short-necked clam, soft tissue	5.6
Indian halibut, muscle	3.9
Crab, muscle	3.1
Silver pomfret, muscle	2.8
Stockholm, Sweden	
Atlantic herring, muscle	36
Common mussel, blue mussel, soft tissue	22
European eel, muscle	2.8
Plaice, muscle	2.5
Atlantic salmon, muscle	Not detected

Table 6-4. Tributyltin (TBT) Levels in Food

Food item	Concentration (ng TBT/g) wet weight
Sydney, Australia	
Slimy mackerel, muscle	13
Sydney rock oyster, soft tissue	9.2
Butterfly fan lobster, muscle (tail)	7.2
Arrow squid, cuttlefish, muscle	7
Tiger flathead, muscle	6
Yellowtail kingfish, muscle	5.3
Largetooth flounder, muscle	4.2
Halifax, Canada	
Longfin inshore squid, muscle	8.9
Cock shrimp, whole body	7.7
Common mussel, soft tissue	5.6
Witch flounder, muscle	2.7
Atlantic salmon, muscle	Not detected
Cock shrimp, tail only	Not detected
London, England	
Oyster, soft tissue	43
Shrimp, muscle	13.9
Atlantic herring, muscle	11
Squid, muscle	7.9
Mackerel, muscle	7.3
Mussel, soft tissue	5.9
Seafood from six markets in the United States[b]	*Reported as mean summer, winter*
San Pedro, California	
Bottom fish	7.1, 1.7
Crustaceans	1.2, 1.1
Mollusks	13, 1.5
Pensacola, Florida	
Bottom fish	2.1, 1.4
Crustaceans	1.0, 1.4
Mollusks	2.0, no data
Chicago, Illinois	
Freshwater fish	5.9, 3.2
Boston, Massachusetts	
Bottom fish	1.3, 1.2
Mollusks	3.1, 0.70
Baltimore, Maryland	
Bottom fish	1.3, 23
Crustaceans	1.2, 1.0
Mollusks	3.3, 0.54

Table 6-4. Tributyltin (TBT) Levels in Food

Food item	Concentration (ng TBT/g) wet weight
Seattle, Washington	
Bottom fish	0.98, 1.0
Crustaceans	2.4, 1.2
Pen-reared fish	5.2, 14

[a] Keithly et al. 1999
[b] Cardwell et al. 1999b

(WHO 2003). Data from the Can Manufacturers Institute (CMI 1988) indicate that >90% of tin-lined cans used for food today are lacquered. Only light colored fruit and fruit juices are packed in unlacquered cans, since tin helps maintain the color of the fruit. Tin content in foods stored in opened metal cans increases over time, since tin can rapidly dissolve in the presence of oxygen. Acidic foods are more aggressive to the tin coating in metal cans, and canned acidic foods have higher tin contents. Tin concentrations of canned foods increase with storage time and temperature (WHO 2003).

Tin concentrations in various foods were determined in a dietary tin intake study for adults in France. Foods in lacquered cans generally were found to contain tin concentrations below 10 mg/kg, and tin concentrations ranged from 24 to 156 mg/kg in food from unlacquered cans. The average tin concentration in fresh foods was 0.03 mg/kg (Biégo et al. 1999). Canned vegetables and fruit products were found to have mean tin concentrations of 44 and 17 mg/kg fresh weight, respectively, in a 1994 total diet study in the United Kingdom (Ysart et al. 1999). A study of metal concentration in canned milk products in Lithuania showed that the content of tin in canned milk exceeded the concentration in raw milk, which, in 1990–1992, was on average 0.22 mg/kg. Mean tin concentrations in evaporated sterilized milk, concentrated sterilized milk, and sweetened condensed milk were 85, 89, and 40 mg/kg, respectively. Tin concentrations in canned milk were shown to increase during storage (Ramonaiytė 2001). Local and imported edible seaweeds obtained in British Columbia were found to contain tin in concentrations ranging from 0.01 to 0.46 mg/kg dry weight (van Netten et al. 2000).

Samples of fish, crustaceans, cephalopods (i.e., squid), and bivalve mollusks were purchased from markets in Stockholm, Sweden; London, England; Marseille, France; Singapore; Ulsan, Korea; Sydney, Australia; Galveston, United States; and Halifax, Canada during August and September 1997 and analyzed for tributyltin content. Average tributyltin concentrations for bivalves, pelagic fish, pelagic invertebrates, and flatfish were 40, 16, 7.4, and 4.6 µg TBT/kg, respectively. It was noted that the high concentrations in bivalves were expected. The lower concentrations of tributyltin found in flatfish were unexpected, since flatfish live on sediment and consume mostly benthic prey. Sediment is considered a sink for tributyltin in aquatic environments (Keithly et al. 1999). In a similar study, seafood was purchased in August 1989 and January 1990, representing a summer and winter sample, from Boston, Massachusetts; Baltimore, Maryland; Seattle, Washington; Pensacola, Florida; San Pedro, California; and Chicago, Illinois. These locations represented major fishing and aquaculture areas on the coasts of the United States and the Great Lakes. Categories of seafood sampled were bottom fish, crustacea, freshwater fish, mollusks, and maricultured fish. Tributyltin was detected in 35% of samples analyzed. Seafood purchased during the summer was found to have slightly higher tributyltin concentrations compared to seafood purchased in the winter in 10 of the 15 instances where the same or similar species were sampled from the same location during the summer and winter surveys. Elevated tributyltin concentrations in seafood sampled during the summer were believed to be consistent with increased recreational boat activity in the summer. Mean tributyltin summer concentrations for bottom fish, crustaceans, and mollusks were 0.98–7.1, 1.0–2.4, and 2.0–13 µg TBT/kg, respectively. Mean tributyltin winter concentrations for the same seafood categories were 1.0–23, 1.0–1.4, and 0.54–6.3 µg TBT/kg, respectively. The respective summer and winter mean concentrations of tributyltin were 5.9 and 3.2 µg TBT/kg in freshwater fish from Chicago, Illinois and 5.2 and 14 µg TBT/kg for pen-reared fish from Seattle, Washington (Cardwell et al. 1999b).

Tributyltin and triphenyltin concentrations were determined in foods in a market basket study. About 100 kinds of foods were purchased every year in 1990–1993 in Shiga Prefecture, Japan. Foods were divided into 13 groups: I, rice; II, cereals, grains, and potatoes; III, sugar and cakes; IV, fats and oils; V, bean products; VI, fruits; VII, green vegetables; VIII, other vegetables and seaweeds; IX, seasonal beverages; X, fish, mollusks, and crustaceans; XI, meats and eggs; XII, milk and dairy products; and XIII, cooked meats (curry and hash). Tributyltin and triphenyltin (TPT) were only detected in group X (fish, mollusks, and crustaceans) and group VIII (vegetables and seaweeds), with higher levels in group X (5.2 µg TBT and 0.4 µg TPT), than in group VIII (0.2 µg TBT and 0 µg TPT) (Tsuda et al. 1995). Twenty-two samples of gin, martini, cognac, red wine, and sherry that were stored in plastic containers, used in Canada for storage of alcoholic beverages, were analyzed for dioctyltin compounds, dioctyltin bis(maleate), and dioctyltin *S*,*S*'-bis(isooctyl mercaptoacetate). Beverages tested contained <40 µg/L tin. While these plastic containers contained up to 1,700 µg Sn/g, and these dioctyltin compounds were soluble in alcohol (64.7 and 150 µg/mL, respectively), there was no evidence of leaching in any samples analyzed (Méranger 1975).

Tin and organotin concentrations found in human tissues and fluids are summarized in Table 6-5. Tin was detected in nine human adipose tissue samples during the 1982 National Human Adipose Tissue Survey at concentrations ranging from 4.6 to 15 µg/g (Stanley 1986). Urine samples were selected from the available archived urine specimens from participants in the National Health and Nutrition Examination Survey (NHANES) III, conducted from 1988 to 1994. The 500 samples were chosen to represent a broad range of the U.S. population. Tin was detected in 89% of samples (detection limit, 0.1 µg/L) and had a 95th upper percentile concentration of 20.1 µg/L (Paschal et al. 1998). Tissue samples from various organs were obtained from 20 deceased individuals (15 men and 5 women), who, at the time of their death, lived in Terragona, Spain and the surrounding areas for at least 10 years. No known

Table 6-5. Tin and Organotin Levels in Human Tissues and Fluids

Human tissue or fluid	Concentration	Units	Reported as	Reference
Tin				
Adipose tissue, (n=9)	4.6–15	µg/g	Range	Stanley 1986
Urine, NHANES, (n=500)	20.1	µg/L	95th upper percentile	Paschal et al. 1998
Urine (n=14) occupationally non-exposed men and women, Germany	1.8 (1.0–2.7)	µg/L	Mean (range)	Schramel et al. 1997
Terragona, Spain (n=20)				
Brain	0.98 (0.28–4.57)	µg/g ww	Mean (range)	Llobet et al. 1998
Bone	6.18 (2.72–17.32)			
Kidney	1.54 (0.68–3.04)			
Liver	4.44 (1.84–10.16)			
Lung	1.74 (0.67–6.54)			
Terragona, Spain (n=78)				
Brain	0.27 (0.23–0.74)	µg/g ww	Mean (range)	García et al. 2001
Bone	0.47 (0.45–0.76)			
Kidney	0.25 (0.23–0.43)			
Liver	0.16 (0.09–0.27)			
Lung	0.24 (0.23–0.31)			
Organotin compounds				
Blood (n=32)				
Central Michigan				
Monobutyltin	0.00817	µg/mL[a]	Mean	Kannan et al. 1999
Dibutyltin	0.00494			
Tributyltin	0.00818			
Liver				
Poland (n=9)				
Total butyltin (MBT+DBT+TBT)	0.0024–0.0110	µg/g ww[a]	Range	Kannan and Falandysz 1997
Denmark (n=18)				
Monobutyltin	0.0003–0.0047	µg/g ww[a]	Range	Nielsen and Strand 2002
Dibutyltin	0.0008–0.0283			
Tributyltin	<0.0003			
Triphenyltin	<0.003			
Japan (n=4)				
Monobutyltin	0.018 (0.012–0.022)	µg/g ww[a]	Mean (range)	Takahashi et al. 1999
Dibutyltin	0.066 (0.045–0.078)			
Tributyltin	<0.0020			

[a] Concentrations of organotins are reported in µg organotin species/g or mL.

DBT = dibutyltin; MBT = monobutyltin; TBT = tributyltin; ww = wet weight occupational exposure to metals was found for these subjects based on a questionnaire sent to relatives. Tin concentrations were lowest in brain tissue and highest in bone at 0.98 and 6.18 μg/g wet weight, respectively. No significant differences in tin concentrations were noted based on gender or age (Llobet et al. 1998). In a similar study, samples of liver, lung, kidney, brain, and bone were collected from 78 adult subjects (57 men and 21 women) autopsied between 1997 and 1999 who at the time of death lived in Tarragona County, Spain or in the surroundings for the last 10 years. Autopsy records included data on gender, age, occupation, residence, and smoking and drinking habits. No occupational exposure to heavy metals was found in this group. Ages ranged from 36 to 76 years, 55% were considered smokers, and 24% were considered drinkers. An individual was considered a smoker if he or she smoked more than one pack of cigarettes per day for at least 1 year of his or her life. Men who consumed more than 280 g of alcohol per week (168 g for women) were considered drinkers. Place of residence was divided into three areas: (a) near the petrochemical industry, (b) near the petroleum refineries and municipal solid waste incinerator, and (c) urban area (downtown). For tin concentrations in the tissues studied, no significant differences between sex, smoking and drinking habits, or places of residence were found. One exception was in the kidney, where tin concentrations were slightly higher in drinkers (García et al. 2001).

Butyltin compounds were measured in human blood collected in July 1998 in central Michigan from 17 male and 15 female individuals. Mono-, di-, and tributyltin were detected in 53, 81, and 70% of the samples. Mono-, di-, and tributyltin concentrations ranged from below the detection limit to maximum concentrations of 0.027, 0.016, and 0.085 μg organotin ion/mL, respectively. Total butyltin concentrations ranged from below the detection limit to 0.101 μg BT/mL (Kannan et al. 1999). Human liver samples from nine individuals, aged 45–83, obtained from the Gdansk School of Medicine, Poland in March 1994, were found to contain total butyltin (mono-, di-, and tributyltin) concentrations ranging from 0.0024 to 0.011 μg BT/g wet weight (Kannan and Falandysz 1997). Four human liver samples obtained by autopsy in Ehime University Hospital, Japan in 1997 and 1998 were found to contain average concentrations of mono-, di-, tributyltin, and total butyltin of 0.018, 0.066, <0.002, and 0.084 μg organotin ion/g wet weight, respectively (Takahashi et al. 1999). Liver samples from 18 deceased Danish men aged 21–82 were collected from December 1999 to January 2000 at the Institute for Forensic Medicine, SDU, Odense University. Concentrations of tributyltin and triphenyltin were all below the detection limit, <0.0003 μg TBT/g and <0.003 μg TPT/g. Mean concentrations (and ranges) of mono- and dibutyltin were 0.0016 (0.0003–0.0047) μg MBT/g and 0.009 (0.0008–0.0283) μg DBT/g wet weight. A large interperson variability was noted for this sample with a more than 25-fold difference between the lowest and highest dibutyltin liver concentration (Nielsen and Strand 2002).

Ten individual indoor dust samples were collected from 10 regions from the United Kingdom in 2002. Samples were collected primarily from private households, but also included some businesses. Samples were analyzed for various chemicals including eight organotin compounds, mono-, di-, tri-, and tetrabutyltin, mono- and dioctyltin, tricyclohexyltin, and triphenyltin. Mono-, di- and tributyltin, and mono- and dioctyltin were found in all pooled regional samples, and mean concentrations were 1.375, 0.563, 0.1445, 0.4506, and 0.1292 μg organotin ion/g, respectively. Triphenyltin was found in only one pooled sample, at a concentration of 0.0069 μg TPT/g. Tetrabutyltin and trihexyltin were not detected. Detection limits were 0.001 μg organotin ion/g dry weight. Possible sources of these organotin compounds in the home may be from the use of butyl- and octyltin compounds as stabilizers in PVC. In addition, tributyltin is used as a fungicide and as treatment against dust-mites in carpets and textiles. Dust samples from Denmark, Finland, France, Spain, and Sweden showed similar patterns of organotin contents as found in the United Kingdom samples (Santillo et al. 2003).

Tin concentrations in the kidneys of mink collected from the Kootenay River and lower Fraser River in British Columbia, Canada were 6.25 and 5.5 μg/g dry weight. Tin concentrations in the livers of mink from the upper and lower Fraser River were 5.53 and 5.17 μg/g dry weight, respectively. Tin concentrations in the livers of otters were <4 μg/g dry weight collected from the Kootenay, lower and upper Columbia, and upper Fraser Rivers, and 2.67 μg/g from the lower Fraser River (Harding et al. 1998). Tin concentrations in mantle muscle and liver samples of juvenile Japanese common squid, *Todarodes pacificus*, collected from three locations in and near Japanese coasts, were 0.042–0.050 and 0.077–0.13 μg/g wet weight, respectively (Ichihashi et al. 2001).

Concentrations of butyltin (mono-, di-, and tributyltin) compounds were determined in the kidney and liver of 18 species of seabirds collected between the mid-1980s and mid-1990s from Japan, Korea, the North Pacific Ocean, and the southern Indian Ocean. The highest mean total butyltin concentrations were found in the kidney and liver of inland and coastal birds. The highest mean concentrations of butyltins (BT) were found in common cormorants from Lake Biwa, Japan at 0.300 and 0.280 μg BT/g wet weight, in kidney and liver, respectively. Among the open sea birds, the Laysan albatross from the North Pacific Ocean had the highest total butyltin concentrations in the liver at 0.043 μg BT/g wet weight (Guruge et al. 1997).

Concentrations of tributyltin and triphenyltin were measured in the muscle of 11 species of fish from the Port of Osaka and Yodo River, Japan. Concentrations of tributyltin and triphenyltin were found ranging from 0.011 to 0.182 µg TBT/g and from <0.001 to 0.130 µg TPT/g wet weight. In addition, mono- and dibutyltin and diphenyltin were detected in all samples. Monophenyltin was detected in all but one sample from the Port of Osaka and none of the samples from the Yoda River (<0.001 µg MPT/g wet weight). Concentrations of organotin compounds were higher in fish from sea areas than those from the river (Harino et al. 2000). Ueno et al. (2004) determined butyltin concentrations in the liver of skipjack tuna (*Katsuwonus pelamis*) collected from Asian offshore waters, off-Seychelles (west African coast), off-Brazil (west South American coast), and in open seas (North Pacific) during 1996–2001. High concentrations of butyltins were found in skipjack tuna from offshore waters around Japan with concentrations up to 0.400 µg BT/g wet weight. Tributyltin was detected a relatively higher concentrations in all locations, with mean concentrations ranging from 0.0049 to 0.200 µg TBT/g wet weight in the North Pacific and the East China Sea, respectively. Monobutyltin concentrations were below the detection limit (0.0018 µg MBT/g) for four samples from the South China Sea, off-Indonesia, off-Seychelles, and off-Brazil, and ranged up to 0.017 µg MBT/g wet weight in the East China Sea (Ueno et al. 2004).

Concentrations of di- and tributyltin were studied in whole-body fish samples from six freshwater sites across the United States (Jones-Lepp et al. 2004). Di- and tributyltin were not detected in 8 and 9 of the 13 fish samples, respectively, that were collected from these sites (detection limits were 0.00097 and 0.0018 µg/g for di- and tributyltin, respectively). The highest concentrations were reported in largemouth bass (*Micropterus salmoides*) from Red Bank Creek, South Carolina at 0.221 µg DBT/g , and in shorthead rosehorse (*Moxostoma macrolepidotum*) from the Little Missouri River, North Dakota at 0.389 µg TBT/g (Jones-Lepp et al. 2004).

Strand and Asmund (2003) studied the concentrations of butyltins in bivalves collected between 1999 and 2000 from six areas along the west coast of Greenland. The highest tributyltin concentration, 0.254 µg TBT/g wet weight, was found in mussels (*Mytilus edulis*) sampled inside Nuuk harbor, the largest harbor in West Greenland. Tributyltin could only be detected in two of the six areas outside of the harbor areas at concentrations of 0.001 and 0.0027 µg TBT/g wet weight, in *Chlamys islandica* and *Nuculana pernula*, respectively. Di- and monobutyltin concentrations ranged from <0.0005 to 0.025 and from <0.0005 to 0.0041 µg organotin ion/g wet weight, respectively, in *M. edulis* in the harbor sites. Di- and monobutyltin were not detected in *C. islandica* from open water sites, and were detected in *N. pernula* from open water at 0.0016 and 0.0012 µg organotin ion/g wet weight, respectively. Triphenyltin could not be detected in any samples (<0.005 µg TPhT/g wet weight) (Strand and Asmund 2003). *M. edulis*, clams (*Mercenaria mercenaria*), and fish (*Tautogolabrus adspersus*) collected in 1995 from Coddington Cove, Newport, Rhode Island were found to contain tributyltin concentrations ranging from 0.0092 to 0.977 µg Sn/g wet weight. Tributyltin concentrations in lobsters from the same area were all below the detection limit (<0.006 µg Sn/g) (Wade et al. 2004). Tributyltin concentrations were measured in benthic mollusks (*N. pernula, Nucula sulcata, Nucula tenuis, Artica islandica, Musculus niger, Cardium echinatum, Buccinum undatum,* and *Neptunea antiqua*) collected in 1997 and 1999 from transects along and perpendicular to the shipping lanes in the Sound (Øresund) and the Kattegat/Skagerrak region, an important shipping strait between Denmark and Sweden. Di- and tributyltin were detected in all mollusk samples, and ranged from 0.011 to 0.267 µg DBT/g and from 0.0081 to 1.316 µg TBT/g dry weight (Strand et al 2003). Tributyltin was found in mussels (*Mytilus galloprovincialis*) from Portuguese coastal waters at concentrations of 0.011–0.789 µg Sn/g dry weight and was detected at all 17 sites sampled between May and July 2000. Mono- and dibutyl tin were also found in most samples with concentrations ranging from not quantifiable to 0.605 and from not quantifiable to 0.345 µg Sn/g dry weight, respectively. Di- and triphenyltin concentrations were not quantifiable in all but one sample, with a triphenyltin concentration of 0.016 µg Sn/g dry weight (Barroso et al. 2004).

Tributyltin, dibutyltin, and monobutyltin concentrations were determined in the liver, kidney, and brain tissues of adult southern sea otters (*Enhydra lutris nereis*) found dead along the coast of California during 1992–1996. The mean and range of liver, kidney, and brain concentrations for total butyltin compounds were 1.320 (0.040–9.2), 0.160 (0.004–0.43), and 0.061 (0.0027–0.14) µg BT/g wet weight, respectively. The accumulation of butyltin compounds in sea otters was explained by their bottom-feeding habit and a diet that consists exclusively of invertebrates such as mollusks and gastropods (Kannan et al. 1998a). Butyltin concentrations in the liver, kidney, and brain tissues of southern sea otters (*E. lutris nereis*) found dead on the California coast during 1992–1996 were 0.040–5.3, 0.004–0.265, and 0.0039–0.140 µg BT/g wet weight, respectively (Kannan et al. 2004).

Berge et al. (2004) studied the concentrations of organotin compounds in samples of harbor porpoise (*Phocoena phocoena*), common seal (*Phoca vitulina*), ringed seal (*Phoca hispida*), and glaucous gull (*Larus hyperboreus*) from Norwegian territories without any obvious point sources of tributyltin. Most samples were collected between 1998 and 2000; however, some of the porpoise samples were collected in 1988, which is prior to the restriction on the use of tributyltin on smaller boats. The highest concentrations of mono-, di-, and tributyltin were found in harbor porpoise samples in Northern Norway in 1988, especially in liver tissue with mean concentrations of 0.0345, 0.285, and 0.098 µg Sn/g wet weight, respectively. In general, mono-, di-, and tributyltin concentrations were lower in harbor porpoise tissues sampled in 1999 than in 1988. No phenyltins were found in ringed seals from Spitsbergen or in glaucous gulls from Bear Island. Concentrations of phenyltins in blubber, kidney, and brain of common seals were below the detection limit (generally <0.001 µg Sn/g wet weight). Mono-, di-, and triphenyltin were detected in the liver, muscle, and kidney of harbor porpoises samples in 1999; mono- and diphenyltin were dominant in liver and muscle with mean concentrations of 0.0164 and 0.0192 µg Sn/g wet weight, respectively (Berge et al. 2004).

Ciesielski et al. (2004) measured the organotin concentrations in liver tissue of marine mammals found between 1999 and 2003 from the Polish coast of the Baltic Sea. The mammals studied included 14 harbor porpoises (*P. phocoena*), 2 striped dolphins (species not specified), 1 ringed seal (*P. hispida*), and 2 grey seals (*Halichoerus grypus*). Tributyltin was detected in all samples and ranged from 0.044 to 1.488 µg Sn/g dry weight in grey seal and striped dolphin, respectively. Dibutyltin was not detected in the two grey seal liver samples, but was detected in all other samples ranging from 0.071 to 3.295 µg Sn/g dry weight in ringed seal and striped dolphin, respectively. Monobutyltin was not detected in one of the grey seal samples, but was detected in all other samples ranging from 0.021 to 2.915 µg Sn/g dry weight for grey seal and striped dolphin, respectively (Ciesielski et al. 2004).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Human exposure to tin may occur by inhalation, ingestion, or dermal contact. However, exposure of the general population occurs primarily by ingestion of food (NAS 1977; WHO 1980). The daily intake from air is unlikely to exceed 0.5 µg based on concentrations of tin in air that have been estimated to be in the range of 0.002–0.03 µg/m^3 (Biégo et al. 1999). Tinplate, which is steel coated with a thin layer of metallic tin, has been used to line cans for food. Some of these cans are also coated with a lacquer. While new canning techniques have decreased the amount of tin contamination of foods over the years, metal cans still are the main source of tin in the diet (WHO 2003). Tin(II) chloride is used as a food additive and has U.S. FDA Generally Regarded As Safe (GRAS) approval. It is used as a preservative for canned soda water, a color retention agent in canned asparagus, and a component in food packaging materials (Kroschwitz and Howe 1997). Tin exposure may occur from dental preparations, since tin(II) fluoride (0.41%) is an approved fluoride source in dentifrices (Pader 1993). In a laboratory study to determine the amount of tin and other metals leached into water from copper piping with four types of lead-free solders, which contain 94–95.5% tin, no significant leaching of tin was observed (Subramanian et al. 1991).

Estimates of daily dietary tin intake ranged from 1 mg, for diets consisting mainly of fresh meats, vegetables, and cereals, to 38 mg for diets including a high proportion of canned foods (Schafer and Femfert 1984; WHO 1980). The average daily tin intake of an adult in the United States was estimated at 4.003 mg (4 mg from food and 0.003 mg from air), and with undetectable levels contributed by drinking water (EPA 1987a; WHO 1980). Other estimates of human daily intake range from 0.2 to 17 mg (Klaassen et al. 1986; Krigman and Silverman 1984). Tin levels in drinking water have been reported at <0.010 mg/L. If daily intake of water is assumed to be 2 L/day, then intake of tin from water would be 0.012–0.020 mg/day (WHO 2003). The tin contents in fresh food or food packaged in lacquered or unlacquered cans were determined to estimate the daily tin intake in an adult in France. From this study, it was found that canned foods, while representing 6–7% of the daily consumed foods, represented >95% of the total tin intake. The estimated tin intake by an adult in France was determined to be 0.04 mg/kg body weight (Biégo et al. 1999). In a 1994 total diet study in the United Kingdom, the canned vegetables group and fruit product group contributed 66 and 31%, respectively, to the total average exposure of tin, which was estimated as 2.4 mg/day. From this study, an upper range exposure to tin of 7.9 mg/day was estimated. Population dietary exposure to tin from total diet studies in the United Kingdom from 1976 to 1994 ranged from 1.7 mg/day in 1985 to 5.4 mg/day in 1991 (Ysart et al. 1999).

Little is known about the extent of exposure of humans to butyltin compounds (Kannan et al. 1999). Occupational exposure represents the greatest exposure to tributyltin; nonoccupational exposure to tributyltin is usually slight, with diet as the most important means of exposure (Demora and Pelletier 1997). Dermal absorption is a significant route of occupational exposure for certain organotin compounds (Stewart and Lassiter 2001). Household commodities made of polyurethane, plastic polymers, and silicons contain butyltin concentrations in the ppm range. Butyltin compounds are also found in seafood (Cardwell et al. 1999b; Kannan et al. 1999; Keithly et al. 1999). The daily intakes of tributyltin and triphenyltin in Japan were estimated to be 4.7 and 0.7 μg in 1991 and 2.2 and 0.7 μg in 1992, respectively, based on a duplicate portion study. In this study, cooked meals were collected for 3 days from women in Shiga Prefecture, Japan in 1991 and 1992, and were homogenized and frozen. In a separate market basket study in Shiga Prefecture, Japan, daily intakes of tributyltin and triphenyltin in Japan were estimated to be 6.9 and 5.4 μg in 1991 and 6.7 and 1.3 μg in 1992, respectively. Of the food groups analyzed in the market basket study, 95% of the daily intakes of tributyltin and triphenyltin came from the fish, mollusks, and crustaceans food group (Tsuda et al. 1995). Human dietary exposure to butyltins by food in order of importance may be regarded as: marine food > animal-origin foods (dairy and meat) > farm products (rice, and sunflower and peanut oil) (Kannan et al. 1995). Other routes of exposure to organotin compounds may include leaching of organotin compounds from PVC and related materials, which have led to contamination of food, drinking water, and municipal sewage sludges, as suggested in some studies. Dibutyltin and octyltin compounds have been found in some textiles products. It has been demonstrated that butyltin compounds in siliconized baking parchment can be transferred to food baked on this type of baking parchment (Takahashi et al. 1999). Organotin compounds were found in household dust in a U.K. study (Santillo et al. 2003).

Occupational exposures to tin may be substantial. Inhalation or dermal exposure to triphenyltin leachate, used in fungicides and insecticides, may occur during both manufacturing and application (NAS 1977; WHO 1980). Workers in the numerous industries producing or using inorganic tin or organotin compounds (Section 5.3) may also be exposed. NIOSH estimated that 730,000 workers in the United States were potentially exposed to tin in the workplace in 1980 (NOES 1989). The National Occupational Exposure Survey (NOES) database does not contain information on the frequency, concentration, or duration of exposure to workers to tin or any of its compounds. These surveys provide only estimates of number of workers potentially exposed to chemicals in the workplace.

6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in Section 3.7, Children’s Susceptibility.

Children are not small adults. A child’s exposure may differ from an adult’s exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child’s diet often differs from that of adults. The developing human’s source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child’s behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Exposure to tin and tin compounds for children will be similar to adults and will occur primarily through the diet. In a 7-day duplicate diet study of 97 pre-school aged (1.75–2.2 years) children from the Birmingham area in the United Kingdom, the average daily intake of tin was 1.78 mg/kg. In this study, mothers were asked to collect and weigh duplicate samples of all food and drink (including water) consumed by their children in and outside of the home. There was a significant correlation between the amount of canned food consumed and the concentration of tin in the diet (Smart et al. 1987). Children living in institutional settings may be served more canned foods due to their ease of storage and economical price, and may be exposed to higher levels of tin than the general population (WHO 2003). In a joint World Health Organization (WHO) and International Atomic Energy Agency (IAEA) collaborative study published in 1989 on minor and trace elements in breast milk, median tin concentrations were 2.81 and 0.24 μg/L in breast milk from women in Guatemala and Zaire, respectively, 3 months after giving birth (WHO/IAEA 1989). No data were located regarding current concentrations of tin or tin compounds in human breast milk in the United States. Other possible exposures to tin by children may occur from the clothing of other household members with occupational exposure (Rinehart and Yanagisawa 1993).

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

People eating a high percentage of their diet from canned foods will be exposed to higher amounts of tin than the general population. For example, people living in intuitional settings, such as nursing homes, boarding schools, or prisons, or people with lower incomes may be served or choose canned foods due to their ease of storage and economical price (WHO 2003).

Potentially high inhalation exposures to tin and its compounds may occur in the workplace or from agricultural uses of tin compounds. A study of the tin and lead concentrations in house dust from the homes of nine electrical-cable splicers employed by a large power company found higher tin concentrations in house dust from the splicers' homes compared to house dust from control homes. Tin concentrations in house dust from the homes of splicers and the controls were 117 and 14 ppm in laundry areas, and in other areas concentrations were 66 ppm and not detected (<10 ppm), respectively. In one of the control homes occupied by a person who soldered copper water pipes in his home using lead-tin solder, tin concentrations in dust were 5 times higher than levels found in dust from homes of either the control or splicer groups (Rinehart and Yanagisawa 1993). In a 1994 study of heavy metal exposure in a Bolivian smelter, personal breathing zone air samples were collected by 15 workers, representing 12 job categories during one shift according to NIOSH Method 7300. Tin exposure was below the occupational exposure criterion and was considered not hazardous (Sussell et al. 1996).

6.8 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of tin and tin compounds is available. Where adequate information is not available, ATSDR, in conjunction with 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 tin and tin compounds.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.8.1 Identification of Data Needs

Physical and Chemical Properties. Table 4-2 and Section 4.2 summarize many of the relevant physical and chemical properties of tin and many of its compounds. There are adequate data for the physical and chemical properties of tin and inorganic tin compounds. The chemical behavior of most of the common organotin compounds in environmentally-relevant media is not well known. There is a need to measure the solubility and vapor pressure of the more important organotin compounds in order to provide a more reliable basis for predicting their fate in the environment.

Production, Import/Export, Use, Release, and Disposal. According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information for 2001, became available in May of 2004. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Production volumes and uses of tin are well-documented (Carlin 2003b, 2004). While data were available on the uses of many organotin compounds, current production volumes could not be located. Data on releases, disposal practices, and possible environmental contamination from uses of tin and its compounds are limited. Since tin is not on the TRI and is not listed as an EPA hazardous waste constituent, current data are not available on industrial releases or disposal practices. Information on releases or disposal practices, and current quantitative data on leaching of inorganic and organic forms of tin into foods from tin-lined cans and PVC packaging materials would be useful in assessing potential human exposure to tin compounds.

Environmental Fate. From the information available, it appears likely that both inorganic and organotin will partition to soils and sediments, and will not volatilize from water (Blunden et al. 1984; Cooney 1988; Fent 1996; Maguire et al. 1983, 1985; WHO 1980). Research on physical and biological processes in water and at sediment-water interfaces would be particularly helpful to more accurately predict the fate of tin compounds released to the environment. Methyltin compounds can be produced in the environment by biomethylation of inorganic tin (Fent 1996). It has been suggested that methylation of butyltin compounds in sediment may lead to mobilization of tin species into the water column and possibly to the atmosphere. However, there is currently no significant evidence of losses of organotin compounds to the atmosphere (Amouroux et al. 2000).

Bioavailability from Environmental Media. Inorganic tin is not well absorbed after inhalation, oral, and dermal exposure. Organotin compounds are somewhat better absorbed by both the inhalation and oral routes (Hiles 1974; Mori et al. 1984). Dermal absorption is a significant route of occupational exposure for certain organotin compounds (Stewart and Lassiter 2001). The daily intakes of tin from air, food, and water are small (WHO 1980). Further study of human intake of organotin compounds from food and water would also be useful. The pH may be an important consideration for the bioavailability of organotin compounds. Bioconcentration studies by Looser et al. (1998) indicated that as pH increases, uptake of organotin compounds increases.

Food Chain Bioaccumulation. It has been established that organotins can be bioconcentrated by aquatic organisms in marine environments (Gomez-Ariza et al. 2001; Harino et al. 2000; Hongxia et al. 1998; Laughlin and Linden 1985; Looser et al. 1998; Maguire et al. 1984; Meador 2000; Suzuki et al. 1998; Tsuda et al. 1986; Waldock and Thain 1983; Yamada and Takayanagi 1992). Similar information for terrestrial ecosystems would be useful. Inorganic tin compounds may also be bioconcentrated, but data are limited (Seidel et al. 1980; Thompson et al. 1972). There is no information available on the potential transfer of inorganic tin or organotin compounds from lower trophic levels to higher levels. This information would be useful because studies have shown that organotin can be bioconcentrated significantly.

Exposure Levels in Environmental Media. Reliable monitoring data for the levels of tin and tin compounds in contaminated media at hazardous waste sites are needed so that the information obtained on levels of tin and tin compounds in the environment can be used in combination with the known body burden of tin and tin compounds to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

Data were obtained regarding tin levels in air (Dannecker et al. 1990; EPA 1982a, 1988c; NAS 1977; Sweet and Vermette 1993; WHO 1980). No monitoring data for concentrations of organotin compounds in air were found. Inorganic tin levels in water are limited to data obtained in the early 1980s (NAS 1977; WHO 1980) and more recent data were not found. Due to its use in marine paints, tributyltin levels, as well as di- and monobutyltin, levels are monitored in water (Gomez-Ariza et al. 2001; Grovhoug et al. 1996; Hall 1988; Harino et al. 1998; Sadiki and Williams 1996, 1999; Sadiki et al. 1996; Yang and Maguire 2000). There have only a few surveys reported that monitor the occurrence of organotin compounds in U.S. freshwaters (Bancon-Montigny et al. 2004; Jones-Lepp et al. 2004). Additional information on inorganic and organotin concentrations in all media, especially air, water, and soil at hazardous waste sites, determined by the most sensitive analytical methods, would be useful in evaluating human exposure to tin.

Several estimates concerning the human daily intake of tin have been reported (Biégo et al. 1999; EPA 1987c; Klaassen et al. 1986; Krigman and Silverman 1984; WHO 1980; Ysart et al. 1999). Data on the intake of organotin compounds from food are limited (Cardwell et al. 1999b; Keithly et al. 1999; Méranger 1975; Tsuda et al. 1995).

Exposure Levels in Humans. Tin has been detected in human adipose tissue (Stanley 1986), urine (Paschal et al. 1998; Schramel et al. 1997), and brain, bone, kidney, liver, and lung (García et al. 2001; Llobet et al. 1998). Butyltin compounds have been detected in blood (Kannan et al. 1999) and liver (Kannan and Falandysz 1997; Nielsen and Strand 2002; Takahashi et al. 1999). These reports are for populations without documented high exposures to tin and tin compounds and should represent background levels in human tissues. Biological monitoring data, especially for populations near hazardous waste sites, would help to assess human exposure to tin and tin compounds.

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

Exposures of Children. Very little data were found regarding the exposure of children to tin and tin compounds (Smart et al. 1987; WHO 2003; WHO/IAEA 1989). Like adults, the major route of exposure to tin will be through the diet, particularly a diet high in canned foods. Levels of tin and organotin compounds in the tissue and body fluids of children have not been found. Levels of tin in human breast milk have been reported (WHO/IAEA 1998); however, more recent tin concentrations in human breast milk have not been found.

Child health data needs relating to susceptibility are discussed in Section 3.12.2, Identification of Data Needs: Children's Susceptibility.

Exposure Registries. No exposure registries for tin and tin compounds were located. Tin and tin compounds are not currently substances for which a sub-registry has been established in the National Exposure Registry. Tin and tin compounds will be considered in the future when chemical selection is made for sub-registries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to these substances.

6.8.2 Ongoing Studies

The Federal Research in Progress (FEDRIP 2004) database provides additional information obtainable from a few ongoing studies that may fill in some of the data needs identified in Section 6.8.1. These studies are summarized in Table 6-6.

The Organotin Environmental Programme (ORTEP) Association is an international non-profit organization of producers of organotin compounds established in 1978 by companies from the United States, Europe, and Japan. The goals of the ORTEP Association include the promotion and encouragement of the dissemination of scientific and technical information on the environmental effects of organotin compounds (ORTEP 2004). The International Tin Research Institute (ITRI) tin producers announced, in October 20, 2004, a project that will begin in January 2005 that will generate information to increase the understanding of the tin industry, and the applications of tin, as well as the interactions of tin with humans and the environment, including increased scientific understanding of the environmental fate of tin during its use and recycling (Tin Technology 2004).

Table 6-6. Ongoing Studies on Organotin Compounds[a]

Investigator	Affiliation	Research description	Sponsor
Eng G	University of the District of Columbia	Investigation of the environmental fate of triorganotins that leach in the aerobic and anaerobic sediments of D.C. waterways and determination of the toxicity of these compounds on the aquatic biota.	Department of Agriculture
Pannell KH	University of Texas at El Paso	The investigators propose to continue their initially successful study concerning the synthesis and biocidal evaluation of new organotin materials and compounds.	National Institutes of Health

[a] FEDRIP 2004