

## 6. POTENTIAL FOR HUMAN EXPOSURE

### 6.1 OVERVIEW

Boron and boron compounds have been identified in at least 164 of the 1,689 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007). However, the number of sites evaluated for boron and boron compounds is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites containing boron and boron compounds, 163 are located within the United States and 1 is located in Guam (not shown).

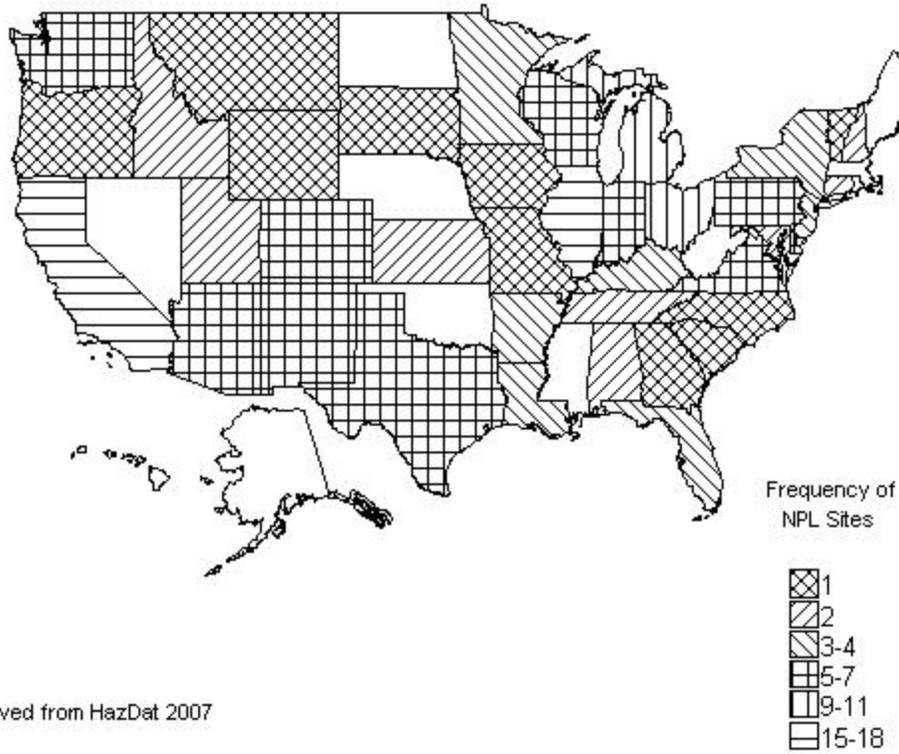
Boron is the 51<sup>st</sup> most common element found in the earth's crust and is found in an average concentration of 8 mg/kg (approximately 0.0008%) (Cotton et al. 1999; Jansen 2003). Boron is a nonmetal and is typically found in nature bound to oxygen. It is never found as the free element (Cotton et al. 1999). There are over 200 minerals containing boron oxide; the four most important boron-containing minerals are borax, kernite, colemite, and ulexite (USGS 2008). Boron is an essential micronutrient for most plants and there is evidence that it is also essential for animals, including humans (Rainey et al. 1999, 2002).

In 2008, the primary use of boron compounds in the United States was for glass and ceramics, followed by soaps and detergents, bleaches, agriculture, and enamels and glazes (USGS 2009). Boric acid is used in cosmetics, pharmaceuticals, and toiletries. It is also used to reduce the flammability of cellulose insulation, cotton batting in mattresses, and wood composites. Boron oxide is also incorporated into cellulose materials to inhibit combustion. Borates are used in the manufacture of adhesives and are added to lubricants, brake fluids, metalworking fluids, water treatment chemicals, and fuel additives (USGS 2008). There are 189 pesticide products registered in the United States that contain boric acid or its sodium salt as an active ingredient (EPA 1993).

Borates are widespread, naturally-occurring substance found mainly as inorganic compounds in sediments and sedimentary rock. Boron is released to the environment slowly in low concentrations by weathering processes. Although few data are available quantifying boron releases from industrial sources, it is estimated that natural weathering releases more boron to the environment worldwide than do these industrial sources (Butterwick et al. 1989).

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**Figure 6-1. Frequency of NPL Sites with Boron and Selected Boron Contamination**



Derived from HazDat 2007

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Boron can be released from municipal sewage waste water, coal-burning power plants, copper smelters, and industries using boron compounds. Boron can also be released from runoff where boron-containing fertilizers and herbicides are used (Butterwick et al. 1989; Fox et al. 2002; Nolte 1988; Waggott 1969).

Adsorption-desorption reactions are expected to be the only significant mechanism that will influence the fate of boron in water (Rai et al. 1986). The extent of boron adsorption depends on the pH of the water and the chemical composition of the soil. The greatest adsorption is generally observed at pH 7.5–9.0 (Keren and Mezuman 1981; Keren et al. 1981; Waggott 1969). The abundance of amorphous aluminum oxide in soil is the single-most important property of soil that will influence the mobility of boron (Bingham et al. 1971).

Rainey et al. (2002) reported mean daily intakes of boron for male and female adults to be 1.28 and 1.00 mg, respectively, from food and beverages. Daily dietary boron intakes were 0.75 mg for infants aged 0–6 months and 0.99 mg for infants aged 7–11 months. Daily boron intakes were 0.86 mg for children aged 1–3 years, 0.80 mg for children aged 4–8 years, 0.90 and 1.02 mg, respectively, for adolescent males aged 9–13 and 14–18 years, and 0.83 and 0.78 mg, respectively, for adolescent females aged 9–13 and 14–18 years.

Ingestion of boron from food (primarily fruits and vegetables) and water is the most frequent route of human exposure, but occupational exposures to boron dusts may be significant. Boron is also a component of several consumer products, including cosmetics medicines and insecticides. Populations residing in areas of the western United States with natural boron-rich deposits may be exposed to higher-than-average levels of boron.

Boron is widely distributed in surface water and groundwater. An average surface water boron concentration in the United States is about 0.1 mg/L (Butterwick et al. 1989; EPA 1986b), but concentrations vary greatly, depending on boron content of local geologic formations and anthropogenic sources of boron (Butterwick et al. 1989). A survey of U.S. surface waters detected boron in 98% of 1,577 samples at concentrations ranging from 0.001 to 5 mg/L (Butterwick et al. 1989). Concentrations of boron in tap water have been reported in a range of 0.007–0.2 mg/L in the United States, Canada, and England (Choi and Chen 1979; Davies 1990; Waggott 1969). In a 1987 survey of 989 public water supplies, boron concentrations ranged from <0.005 to >2 mg/L (NIRS 1987). Mean boron concentrations in soil in the United States are about 30 mg/kg, with concentrations ranging up to 300 mg/kg (Eckel and Langley 1988; USGS 1984).

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**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 2005). This is not an exhaustive list. 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 included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes  $\geq 25,000$  pounds of any TRI chemical or otherwise uses  $>10,000$  pounds of a TRI chemical in a calendar year (EPA 2005).

**6.2.1 Air**

Estimated releases of 3,600 pounds (~1.6 metric tons) of boron trifluoride to the atmosphere from 21 domestic manufacturing and processing facilities in 2006, accounted for about 100% of the estimated total environmental releases from facilities required to report to the TRI (TRI06 2008). Estimated releases of 520 pounds (~0.24 metric tons) of boron trichloride to the atmosphere from five domestic manufacturing and processing facilities in 2006, accounted for about 100% of the estimated total environmental releases from facilities required to report to the TRI (TRI06 2008). These releases for boron trifluoride and boron trichloride are summarized in Tables 6-1 and 6-2, respectively. There is no information on releases of other boron compounds to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997).

Borates are released to air from natural and industrial sources. Natural sources include oceans, volcanoes, and geothermal steam (Graedel 1978). Boron compounds are released from anthropogenic sources such as coal-fired and geothermal steam power plants, chemical plants, and rockets as well as manufacturing

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**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Boron Trifluoride<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	Reported amounts released in pounds per year <sup>b</sup>		
							Total release		
							On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site
AR	1	10	0	0	0	0	10	0	10
DE	1	500	0	0	0	3,770	500	3,770	4,270
FL	1	0	0	0	0	0	0	0	0
LA	3	6	0	0	0	0	6	0	6
MD	1	55	0	0	0	0	55	0	55
NJ	1	0	0	0	0	0	0	0	0
OK	1	1,750	0	0	0	0	1,750	0	1,750
PA	3	0	0	0	0	0	0	0	0
SC	2	11	0	0	4,983	0	11	4,983	4,994
TX	7	2,306	0	0	0	0	2,306	0	2,306
Total	21	4,638	0	0	4,983	3,770	4,638	8,753	13,391

<sup>a</sup>The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

<sup>b</sup>Data in TRI are maximum amounts released by each facility.

<sup>c</sup>Post office state abbreviations are used.

<sup>d</sup>Number of reporting facilities.

<sup>e</sup>The sum of fugitive and point source releases are included in releases to air by a given facility.

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>g</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other on-site landfills, land treatment, surface impoundments, other land disposal, other landfills.

<sup>i</sup>Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

<sup>j</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI07 2009 (Data are from 2007)

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**Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Boron Trichloride<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Reported amounts released in pounds per year <sup>b</sup>							
		Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	Total release		
							On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site
CA	1	0	0	0	0	0	0	0	0
MA	1	0	0	0	0	0	0	0	0
NV	1	0	0	0	0	0	0	0	0
OH	1	0	0	0	0	0	0	0	0
PA	1	0	0	0	0	0	0	0	0
SC	1	35	0	0	2,422	0	2,422	35	2,422
WI	1	35	0	0	0	0	0	35	0
WV	1	0	0	0	0	0	0	0	0
Total	8	70	0	0	2,422	0	2,422	70	2,422

<sup>a</sup>The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

<sup>b</sup>Data in TRI are maximum amounts released by each facility.

<sup>c</sup>Post office state abbreviations are used.

<sup>d</sup>Number of reporting facilities.

<sup>e</sup>The sum of fugitive and point source releases are included in releases to air by a given facility.

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>g</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other on-site landfills, land treatment, surface impoundments, other land disposal, other landfills.

<sup>i</sup>Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

<sup>j</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI07 2009 (Data are from 2007)

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facilities producing fiberglass and other products (EPA 1987; Graedel 1978; Hollis et al. 1988; Lang et al. 1986; Rope et al. 1988; Stokinger 1981).

Boron or boron compounds have been identified in 1 air sample collected from 1,689 current or former NPL hazardous waste sites where it was detected in some environmental media (HazDat 2007).

### 6.2.2 Water

No releases of boron trifluoride or boron trichloride to surface water were reported from 21 and 5 domestic manufacturing and processing facilities, respectively, in 2006 (TRI06 2008). Releases for boron trifluoride and boron trichloride are summarized in Tables 6-1 and 6-2, respectively. There is no information on releases of other boron compounds to surface water from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997).

Boron compounds are released to water in municipal sewage from perborates in detergents and in waste waters from coal-burning power plants, copper smelters, and industries using boron. Borate levels above background may be present in runoff waters from areas where boron-containing fertilizers or herbicides were used (Butterwick et al. 1989; Nolte 1988; Waggott 1969). An average boron concentration of 1 mg/L was reported in sewage effluents in California (Butterwick et al. 1989). Waggott (1969) reported that boron concentrations in municipal sewage in a treatment plant in England ranged from 2.5 to 6.5 mg/L, releasing between 130 and 240 kg boron/day. Matthijs et al. (1999) reported boron concentrations of 0.41–1.2, 0.39–0.96, and 0.44–1.0 mg/L in raw sewage, settled sewage, and effluent, respectively, collected in 1994 from seven Dutch sewage treatment plants. These data demonstrate that boron passes through the sewage treatment process virtually unchanged. Since boron cannot be degraded and is not substantially absorbed during processing, there is almost no removal during the sewage treatment process (Fox et al. 2002).

Boron is also found in water produced from coal bed natural gas produced water (Jackson and Reddy 2007), irrigation, geothermal waste water, and thermal springs (Koç 2007) used for power generation and heating. In the Powder River Basin, Wyoming, boron was detected in coal natural gas waste water outfall and disposal ponds at 5.89–13.08 (0.064–0.14) and 7.72–15.20  $\mu\text{M}$  (0.083–0.16 mg/L), respectively (Jackson and Reddy 2007). In the Great Menderes Basin, Turkey, boron is brought to the surface and released from natural borate mineral deposits into local rivers via geothermal waste waters and crop

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irrigation canals (Koç 2007). The hot waste waters of a geothermal power plant released into the Buyuk Menderes River contained approximately 25–30 mg/L boron (Akar 2007).

Boron or boron compounds have been identified in 100 groundwater and 57 surface water samples collected from 1,689 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2007).

### 6.2.3 Soil

Estimated releases of 1,300 pounds (~0.59 metric tons) of boron trifluoride to soil and 6 pounds (3 kilograms) by underground injection from 21 domestic manufacturing and processing facilities in 2006, accounted for about 100% of the estimated total environmental releases from facilities required to report to the TRI (TRI06 2008). Estimated releases of 136 pounds (61.7 kg) of boron trichlorideto soil and 18 pounds (8.2 kilograms) by underground injection from five domestic manufacturing and processing facilities in 2006, accounted for about 100% of the estimated total environmental releases from facilities required to report to the TRI (TRI06 2008). These releases for boron trifluoride and boron trichloride are summarized in Tables 6-1 and 6-2, respectively. There is no information on releases of other boron compounds to soil or by underground injection from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997).

Boron is naturally released to soil and water by rainfall, weathering of boron-containing minerals, desorption from clays, and decomposition of boron-containing organic matter. Human-made sources include application of boron-containing fertilizers or herbicides, application of fly ash or sewage sludge as a soil amendment, the use of waste water for irrigation, or land disposal of boron-containing industrial wastes (Butterwick et al. 1989; Hollis et al. 1988; Mumma et al. 1984; Nolte 1988; Rope et al. 1988). In the Great Menderes Basin, Turkey, the hot waste waters of a geothermal power plant contained high levels of boron (~25–30 mg/L). This water becomes part of the irrigation systems and is thus deposited in sediments and soils. The boron concentrations of surrounding irrigated soils before the waste water discharges began were 0.15 ppm (0–20 cm depth) and 0.19 ppm (80–100 cm depth), while after the discharges, the boron concentrations were 13.90 ppm (0–20 cm depth) and 3.66 ppm (80–100 cm depth) (Akar 2007). Barber et al. (2006) reported that daily loads of boron in the Boulder Creek, Colorado of 0–55 kg/day are mostly due to the effluent of the Boulder waste water treatment plant. Mumma et al. (1984) reported that the boron concentration in sewage sludges from 23 U.S. cities ranged from 7.1 to 53.3 mg/kg. Landfilling or land application is a common disposal method for these sludges.

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Boron or boron compounds have been identified in 37 soil and 21 sediment samples collected from 1,689 NPL hazardous waste sites, where it was detected in some environmental media (HazDat 2007).

### 6.3 ENVIRONMENTAL FATE

#### 6.3.1 Transport and Partitioning

Boron is generally found in nature bound to oxygen and is never found as the free element (Cotton et al. 1999). Atmospheric boron may be in the form of particulate matter or aerosols as borides, boron oxides, borates, boranes, organoboron compounds, trihalide boron compounds, or borazines. Borates are relatively soluble in water, and will probably be removed from the atmosphere by precipitation and dry deposition (EPA 1987). The half-life of airborne particles is usually on the order of days, depending on the size of the particle and atmospheric conditions (Nriagu 1979). No specific information on the fate of atmospheric boron was located.

Boron readily hydrolyzes in water to form the electrically neutral, weak monobasic acid, boric acid ( $\text{H}_3\text{BO}_3$ ), and the monovalent ion,  $\text{B}(\text{OH})_4^-$ . In concentrated solutions, boron may polymerize, leading to the formation of complex and diverse molecular arrangements. Rai et al. (1986) concluded that because most environmentally relevant boron minerals are highly soluble in water, it is unlikely that mineral equilibria will control the fate of boron in water. Boron was found to not be significantly removed during the conventional treatment of waste water (Matthijs et al. 1999; Pahl et al. 2001; Waggott 1969). Boron may, however, be co-precipitated with aluminum, silicon, or iron to form hydroxyborate compounds on the surfaces of minerals (Biggar and Fireman 1960).

Waterborne boron may be adsorbed by soils and sediments. Adsorption-desorption reactions are expected to be the only significant mechanism that will influence the fate of boron in water (Rai et al. 1986). The extent of boron adsorption depends on the pH of the water and the chemical composition of the soil. The greatest adsorption is generally observed at pH 7.5–9.0 (Keren and Mezuman 1981; Keren et al. 1981; Waggott 1969). Bingham et al. (1971) concluded that the single most important property of soil that will influence the mobility of boron is the abundance of amorphous aluminum oxide. The extent of boron adsorption has also been attributed to the levels of iron oxide (Sakata 1987), and to a lesser extent, the organic matter present in the soil (Parks and White 1952), although other studies (Mezuman and Keren 1981) found that the amount of organic matter present was not important.

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The adsorption of boron may not be reversible in some soils. The lack of reversibility may be the result of solid-phase formation on mineral surfaces (Rai et al. 1986) and/or the slow release of boron by diffusion from the interior of clay minerals (Griffin and Burau 1974).

Partition coefficients such as adsorption constants describe the tendency of a chemical to partition from water to solid phases. Adsorption constants for inorganic constituents such as boron cannot be predicted *a priori*, but must be measured for each soil-water combination. Compilations of available data for boron are given elsewhere (Rai et al. 1986). In general, boron adsorption will be most significant in soils that contain high concentrations of amorphous aluminum and iron oxides and hydroxides such as the reddish Ultisols in the southeastern United States.

It is unlikely that boron is bioconcentrated significantly by organisms from water. A bioconcentration factor (BCF) relates the concentration of a chemical in the tissues of aquatic and terrestrial animals or plants to the concentration of the chemical in water or soil. The BCFs of boron in marine and freshwater plants, fish, and invertebrates were estimated to be <100 (Thompson et al. 1972). Experimentally measured BCFs for fish have ranged from 52 to 198 (Tsui and McCart 1981). These BCFs suggest that boron is not significantly bioconcentrated.

### 6.3.2 Transformation and Degradation

#### 6.3.2.1 Air

There is no information available that suggests that particulate boron compounds are transformed or degraded in the atmosphere. Particulate-phase boron compounds would be removed from the atmosphere by wet and dry deposition. Volatile boron trihalides are moisture sensitive and will hydrolyze to boric acid and their corresponding halogen acid (Culver et al. 1994b).

#### 6.3.2.2 Water

As an element, boron itself cannot be degraded in the environment; however, it may undergo various reactions that change the form of boron (e.g., precipitation, polymerization, and acid-base reactions) depending on conditions such as its concentration in water and pH. In nature, boron is generally found in its oxygenated form (Cotton et al. 1999). In aqueous solution, boron is normally present as boric acid and

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borate ions, with the dominant form of inorganic boron in natural aqueous systems as undissociated boric acid (Choi and Chen 1979). Boric acid acts as an electron acceptor in aqueous solution, accepting an hydroxide ion from water to form  $(\text{B}(\text{OH})_4)^-$  ion. In dilute solution, the favored form of boron is  $\text{B}(\text{OH})_4^-$  (Cotton et al. 1999). In more concentrated solutions ( $>0.1$  M boric acid) and at neutral to alkaline pH (6–11), polymeric species are formed (e.g.,  $\text{B}_3\text{O}_3(\text{OH})_4^-$ ,  $\text{B}_5\text{O}_6(\text{OH})_4^-$ ,  $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ , and  $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ ) (Choi and Chen 1979; Cotton et al. 1999).

### 6.3.2.3 Sediment and Soil

Most boron compounds are transformed to borates in soil due to the presence of moisture. Borates themselves are not further degraded in soil. However, borates can exist in a variety of forms in soil (see Section 6.2.3). Borates are removed from soils by water leaching and by assimilation by plants.

## 6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to boron depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of boron 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 boron 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 boron in a variety of environmental media are detailed in Chapter 7.

### 6.4.1 Air

Boron concentrations in ambient air samples have been reported to range from  $<5 \times 10^{-7}$  to  $8 \times 10^{-5}$   $\text{mg}/\text{m}^3$ , with an average concentration of  $2 \times 10^{-5}$   $\text{mg}/\text{m}^3$  (Howe 1998). Bertine and Goldberg (1971) estimated that approximately 11,600 tons of boron are injected into the atmosphere as a component of fly ash produced by coal combustion, which was estimated to contain an average boron concentration of about 75  $\text{mg}/\text{kg}$ . Mean dust concentrations ranging from 3.3 to 18  $\text{mg}$  particulates/ $\text{m}^3$  were measured in air samples from U.S. facilities where borax was packaged and shipped (Culver et al. 1994a). Dust samples in these facilities were predominantly composed of various types of borates and ranged from 11.8 to 15.2% boron by weight.

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**6.4.2 Water**

Boron is widely distributed in surface water and groundwater. The average surface water boron concentration in the United States is about 0.1 mg/L (Butterwick et al. 1989; EPA 1986b), but concentrations vary greatly, depending on boron content of local geologic formations and anthropogenic sources of boron (Butterwick et al. 1989). A survey of U.S. surface waters detected boron in 98% of 1,577 samples at concentrations ranging from 0.001 to 5 mg/L. Mean boron concentrations calculated for the 15 drainage basins in the continental United States ranged from 0.019 mg/L in the Western Great Lakes Basin to 0.289 mg/L in the Western Gulf Basin (Butterwick et al. 1989). Mean boron concentration ranging from 0.28 to 7.8 mg/L were reported in samples collected during 1985–2002 from 26 sites in the San Joaquin River, California (Hall et al. 2004). The concentration of boron in sea water is about 4.5 mg/L (Butterwick et al. 1989; EPA 1986b).

Several studies have measured boron concentrations in water in those areas of California with boron-rich deposits. Reported high boron concentrations in surface waters ranged from 15 mg/L in coastal drainage waters to 360 mg/L in a boron-rich lake (Butterwick et al. 1989; Deverel and Millard 1988). Mean boron concentration in a California river ranged from 0.30 to 0.50 mg/L over a 20-year period (Butterwick et al. 1989). Reported boron concentrations in groundwater in the San Joaquin Valley ranged from 0.14 to 120 mg/L with a median concentration of about 4 mg/L (Butterwick et al. 1989; Deverel and Millard 1988). Waggott (1969) reported that groundwater boron concentrations >100 mg/L are common in California.

Drinking water surveys generally do not report boron concentration. Concentrations of boron in tap water have been reported in a range of 0.007–0.2 mg/L in the United States and England (Choi and Chen 1979; Waggott 1969), and the National Inorganics and Radionuclides Survey completed in 1987 reported relatively widespread occurrence of boron in 989 public water supplies (NIRS 1987). Boron concentrations ranged from <0.005 to >2 mg/L, with concentrations of up to 0.4 mg/L in 90% of systems (NIRS 1987). A survey of 969 public water supply systems showed that 99% contained boron at <1 mg/L. The maximum level measured was 3.28 mg/L (McCabe et al. 1970). Davies (1990) reported an average boron concentration of 0.0258 mg/L in drinking water from Toronto, Canada (1978–1984).

**6.4.3 Sediment and Soil**

Background boron levels in U.S. soils were reported at a geometric mean concentration of 26 mg/kg with a maximum concentration of 300 mg/kg (Eckel and Langley 1988). Similar concentrations were reported

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in a U.S. Geological Survey report (USGS 1984), with an average boron concentration of 33 mg/kg (range <20–300 mg/kg) in surface soils from the conterminous United States. Mean boron concentrations in soil collected in the summer of 1981 from the Idaho National Engineering Laboratory and a reference site were 10.1 and 4.7 mg/kg dry weight, respectively (Rope et al. 1988). A geometric mean boron concentration of 8.98 mg/kg (range 2.90–38.0 mg/kg) was reported in soil collected from Aviles, northern Spain (Ordonez et al. 2003).

Boron is an essential nutrient for plants. Boron soil concentrations for optimum plant growth reportedly range from 0.1 to 0.5 mg/kg for several plant species (Butterwick et al. 1989).

Geometric mean boron concentration in sediment collected in 1993 and 1994 from 16 Great Lake embayments and riverine environments of eastern Lake Erie, southern Lake Ontario, and the Niagara River ranged from 0.5 to 7.9 mg/kg dry weight (Lowe and Day 2002). Boron concentrations in sediments collected in 1992 from the Neosho River Basin in Kansas ranged from 2 to 6.5 mg/kg dry weight (Allen et al. 2001).

#### 6.4.4 Other Environmental Media

Boron concentrations in various foods are summarized in Table 6-3. Rainey et al. (1999, 2002) reported the highest content of boron in foods such as raisins, peanut butter, peanuts, dried fruits, and avocados with concentrations of 2.20, 1.45, 1.70, 1.87, and 1.22 mg/100 g food, respectively. The top two items that contribute to boron intake were coffee and milk, due to the volume with which they are consumed (Rainey et al. 1999, 2002). Hunt et al. (1991) determined boron concentrations various foods. In general, boron concentrations were lowest in foods such as meats, cereal and grain products, and confections, ranging from  $\leq 0.015$  mg/kg in many of these foods to 1.470 mg/kg in grape jelly. Fruits, vegetables, herbs, and spices contained the highest concentrations of boron, including parsley flakes (26.878 mg/kg), ground cinnamon (10.370 mg/kg); dried onion flakes (6.573 mg/kg), and applesauce (2.828 mg/kg). Meacham and Hunt (1994) studied the boron content in infant (6–11 months) foods. Foods containing fruit typically had the highest concentrations of boron: prunes with tapioca (2.6 mg/kg); apples with ham (2.5 mg/kg); applesauce with apricot (2.5 mg/kg); pears (1.9 mg/kg); and applesauce (1.8 mg/kg). Boron

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**Table 6-3. Boron Levels in Food**

Food item	Level ( $\mu\text{g}/100\text{ g}$ ) <sup>a</sup>
Fruits and vegetables	
Apples, raw	360
Applesauce, unsweetened	280
Avacado, guacamole	1,222 <sup>b</sup>
Bananas, raw	135
Beans, string, cooked	120
Broccoli, boiled	250
Cantaloupe, raw	180
Carrots, raw or frozen	140
Coleslaw with dressing	120
Corn, yellow, cooked	46
Fruit cocktail, canned in heavy syrup	240
Fruit, dried	1,870
Grapes, raw	490
Lettuce, raw	105
Onions, raw	190
Oranges, raw	260
Peaches, raw	530
Pears, raw	280
Peas, green, cooked	130
Potatoes, not fried	62 <sup>b</sup>
Raisins	2,200
Spinach, boiled	180
Tomatoes, raw	63
Beverages	
Apple juice	180
Beer	12
Coffee, from ground beans	29
Fruit-flavored drink from powder	16
Grape juice unsweetened	300
Milk, whole	18
Orange juice	72
Soft drink, cola-type	13
Tea, leaf, brewed	9
Wine, table, dry	610

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**Table 6-3. Boron Levels in Food**

Food item	Level ( $\mu\text{g}/100\text{ g}$ ) <sup>a</sup>
<b>Meat/fish products</b>	
Beef and vegetable stew	120
Beef, burgers	23 <sup>b</sup>
Beef vegetable soup with potato, stew type	140
Chicken breast, broiled, without skin	27
Chili con carne, with beans	170
Hamburger, with tomato and/or ketchup	51
Tuna, canned, water packed	54
<b>Other</b>	
Beans, lima, dry cooked, fat added	370
Beans, refried	400
Bran flakes with raisins	450
Bread, white	46
Cakes	100 <sup>b</sup>
Cereal, ready to eat	128 <sup>b</sup>
Cookies, brownies	112 <sup>b</sup>
French fries, from frozen, deep fried	110
Donuts, sweet rolls, etc.	69
Ice cream, regular, not chocolate	22
Nuts/seeds, whole	1214 <sup>b</sup>
Pasta	44 <sup>b</sup>
Peanut butter	1,450
Peanuts, roasted, salted	1,700
Peas, black-eyed, cooked, fat added	65
Pizza with meat, thin crust	490
Potato chips	325
Rice, white, cooked	32
Spaghetti sauce	120
Spaghetti with meat sauce	65
Tomato sauce	132 <sup>b</sup>

<sup>a</sup>Rainey et al. 1999 (CSFII 1989–1991), unless otherwise noted.<sup>b</sup>Rainey et al. 2002 (CSFII 1994–1996)

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is also found in infant formula (120 µg/L) and expressed human breast milk (10–100 µg/L) (Hunt and Meacham 2001; Hunt et al. 2004, 2005; Lopez-Garcia et al. 2009).

Minoia et al. (1994) determined the concentrations of various elements in beverages available in Italy. Mean boron concentrations in wine, mineral water, beer, ready-to-drink-infusion of tea, and instant coffees were 1.164, 0.112, 0.166, 0.219, and 0.085 mg/L, respectively. In this study, it was estimated that beverages contributed 34% to the estimated weekly total dietary intake of 9 mg of boron (Minoia et al. 1994). Red and white Australian wine samples that were analyzed contained boron concentrations of approximately 2.5 mg/L (Cozzolino et al. 2008).

Boric acid, anhydrous sodium tetraborate, and sodium tetraborate decahydrate (borax) are found in various commercial products including pesticides, plant foods, household cleaners, laundry detergents, facial creams and cleaners, shampoo, diaper rash ointments, and pet products. Typical amounts of borax in detergents range from 1 to 5%. Boric acid concentrations in various ant and roach pesticide products range from 5 to 100% (NIH 2004).

Gonzales et al. (2004) determined elements found in dust collected from homes of Native Americans in Zuni Pueblo, New Mexico where jewelry was produced. Surface dust samples were collected from work and living areas of jewelers' homes and from control homes. A surface area of 715 cm<sup>2</sup> was wiped at each location. Mean boron concentrations were found to be significantly higher in work areas (0.87 µg/sample) than in living areas (0.28 µg/sample) of homes where jewelry was made. The geometric mean boron concentration was 0.19 µg/sample in living areas of homes in which no jewelry was made (Gonzales et al. 2004).

The geometric mean boron concentration in soft tissues of zebra mussels collected in 1993 and 1994 from 16 Great Lake embayments and riverine environments of eastern Lake Erie, southern Lake Ontario, and the Niagara River ranged from 0.92 to 6.89 µg/g dry weight (Lowe and Day 2002). Boron was not detected (detection limit 2–4 µg/g dry weight) in the soft tissues of mussels collected in 1991 or in fish composites collected in 1990–1992 from the Neosho River Basin in Kansas (Allen et al. 2001).

## 6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Human exposure to borates may occur through ingestion of food and water or insecticides used to control cockroaches, inhalation of boron-containing powders or dusts, or the use of boron from cosmetics or

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medical preparations. The most appreciable boron exposure to the general population is likely to be ingestion of food and to a lesser extent in water (Beyer et al. 1983; Waggott 1969). As boron is a natural component of the environment, individuals will have some exposure from foods and drinking water.

Dietary intakes of boron in children and adults in the United States are summarized in Table 6-4. Rainey et al. (1999) reported mean daily intakes of boron for male and female adults to be 1.17 and 0.96 mg/day, respectively (range 0.02–>9 mg/day). The highest median boron intake of 1.30 mg/day was found for adult male vegetarians, and the lowest median boron intake of 0.72 mg/day was found for women aged 19–30 years. Median boron intakes were higher in adult male and female vegetarians, 1.47 and 1.29 mg/day, respectively, than for all adult males and females, 1.17 and 0.96 mg/day, respectively (Rainey et al. 1999). Consumption of fruits and vegetables contribute largely to boron intake in the human diet. An average daily intake of 1 mg was reported for boron for individuals in the United States. Consumption of wine may contribute an additional 3–4 mg/day of boron (Pahl et al. 2001).

Concentrations of various elements were determined in hair samples from women in two areas (acid and alkaline) of southern Sweden (Rosborg et al. 2003). Median boron concentrations were 281 and <1 mg/kg in hair samples from the acid and alkaline areas, respectively. In this study, the boron levels in drinking water were similar, 10.6 and 9.3 µg/L, in the acid and alkaline areas, respectively, and the authors noted that drinking water did not explain the significantly higher concentrations of boron in the individuals living in the acid area (Rosborg et al. 2003). A mean boron concentration of 0.50 mg/kg wet weight was reported in lung tissue collected from 26 nonsmoking individuals, aged >50 years with no history of occupational exposure to elements living in Terni, central Italy (Alimonti et al. 1992). Boron was not detected in a national survey of human adipose tissue (EPA 1986a).

Occupational exposure to boron compounds may be higher. Workers in other industries, including manufacture of glass wool (Jensen 2009), fiberglass and other glass products, cleaning and laundry products, fertilizers, pesticides, and cosmetics, may also be exposed to boron compounds (Stokinger 1981). Culver et al. (1994a) reported average end-of-shift boron concentrations in blood and urine of 0.11–0.26 µg/g and 3.16–10.72 µg/mg creatinine, respectively, collected from workers at a facility where borax is packaged and shipped. Average boron concentrations in blood and urine collected Monday morning prior to the first shift of the week were 0.09 µg/g and 2.75 µg/mg creatinine, respectively (Culver et al. 1994a). In 2004, workers from Kuandian City, China with occupations in boron mines or processing plants producing borax or boric acid were monitored over a 24-hour period for boron

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**Table 6-4. Dietary Boron Intake**

Age group	1989–1991 <sup>a</sup>	1994–1996 <sup>b</sup>
	Mean±standard deviation (mg/day)	
School aged male and female children		
4–8 years (n=993 <sup>a</sup> , 1,650 <sup>b</sup> )	0.85±0.040	0.80±0.01
9–13 years (n=943 <sup>a</sup> , 552 <sup>b</sup> males) (n=560 <sup>b</sup> females)	0.91±0.45	0.90±0.03 (m) 0.83±0.03 (f)
14–18 years (n=759 <sup>a</sup> , 446 <sup>b</sup> males) (n= 436 <sup>b</sup> , females)	0.88±0.47	1.02±0.04 (m) 0.078±0.04 (f)
Adult males (≥19 years ) (n=3,433 <sup>a</sup> , 4,817 <sup>b</sup> )	1.17±0.65	1.28±0.02
19–30 years (n=878 <sup>a</sup> , 853 <sup>b</sup> )	1.07±0.64	1.15±0.03
31–50 years (n=1,297 <sup>a</sup> , 1,684 <sup>b</sup> )	1.17±0.64	1.33±0.03
51–70 years (n=884 <sup>a</sup> , 1,606 <sup>b</sup> )	1.28±0.67	1.34±0.02
>70 years (n=374 <sup>a</sup> , 674 <sup>b</sup> )	1.19±0.61	1.25±0.03
Vegetarian (n=49 <sup>a</sup> )	1.47±0.70	No data
Adult females (≥19 years ) (n=4,881 <sup>a</sup> , 4,536 <sup>b</sup> )	0.96±0.55	1.00±0.01
19–30 years (n=1,199 <sup>a</sup> , 760 <sup>b</sup> )	0.86±0.55	0.87±0.03
31–50 years (n=1,734 <sup>a</sup> , 1,614 <sup>b</sup> )	0.96±0.55	1.00±0.02
51–70 years (n=1,220 <sup>a</sup> , 1,539 <sup>b</sup> )	1.05±0.55	1.11±0.02
>70 years (n=728 <sup>a</sup> , 623 <sup>b</sup> )	0.97±0.52	0.98±0.03
Vegetarian (n=130 <sup>a</sup> )	1.29±1.12	No data
Pregnant women (n=130 <sup>a</sup> , 70 <sup>b</sup> )	1.01±0.72	1.16±0.09

<sup>a</sup>Rainey et al. 1999 (CSFII 1989–1991)<sup>b</sup>Rainey et al. 2002 (CSFII 1994–1996)

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exposure. Total daily boron measured in food, fluids, and personal air averaged 41.2 mg/day for workers in the boron industry, 4.3 mg/day in the surrounding community, and 2.3 mg/day for the comparison group. Blood, post-shift urine, and semen levels of boron determined for the boron industry workers were 19.3, 499.2, and 793.9 mg/day, respectively while the comparison group only had 1.7, 48.0, and 215.0 mg/day, respectively (Xing et al. 2008).

Workers in other industries, including manufacture of fiberglass and other glass products, cleaning and laundry products, fertilizers, pesticides, and cosmetics, may also be exposed to boron compounds (Stokinger 1981). Reported concentrations of borax dust in different areas of a large borax mining and refining plant ranged from 1.1 to 14.6 mg/m<sup>3</sup> for total particulate (Garabrant et al. 1985) and the mean boric acid/boron oxide dust concentration in a boric acid manufacturing plant was 4.1 mg/m<sup>3</sup> for total particulate (Garabrant et al. 1984). Mean dust concentrations ranging from 3.3 to 18 mg particulates/m<sup>3</sup> were measured in air samples from U.S. facilities where borax was packaged and shipped (Culver et al. 1994a). Dust samples in these facilities were predominantly composed of various types of borates and ranged from 11.8 to 15.2% boron by weight. In another study of dust concentrations in air samples from a U.S. borax production facility, mean total dust concentrations ranged from 0.29 to 18.95 mg particulates/m<sup>3</sup>, with average percent boron contents in dust ranging from 5.6 to 10.1% (Woskie et al. 1994).

NIOSH estimated that the number of workers potentially exposed to boron increased from 6,500 in the early 1970s (NOHS 1989) to 35,600 in the early 1980s (NOES 1989). Neither the National Occupational Hazard Survey (NOHS) nor the National Occupational Exposure Survey (NOES) databases contain information on the frequency, concentration, or duration of exposures of workers to any of the chemicals listed therein. These surveys provide only estimates of the number of workers potentially exposed to chemicals in the workplace. Sittig (1985) reports that NIOSH estimated that the numbers of workers potentially exposed to borax, boron oxide, and boron trifluoride are 2,490,000, 21,000, and 50,000, respectively.

## 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.

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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 boron for children will be similar to adults and will occur primarily through the diet. As boron is a natural component of the environment, children, as with the general population, will have some exposure from foods and drinking water. Rainey et al. (2002) reported that average daily boron intakes ranged from 0.75 to 0.99 mg in infants and children aged 0–8 years. In adolescent males and females aged 9–18 years, average daily boron intakes were 0.9–1.02 and 0.78–0.83 mg, respectively. A daily boron intake of 1.16 mg was reported for pregnant women. Dietary intake of boron in children in the United States is summarized in Table 6-4. Meacham and Hunt (1994) reported a daily intake of 0.333 mg for infants (6–11 months) from baby foods and beverages.

Children and infants may be exposed to boric acid or its sodium salts in homes where pesticide products containing boric acid or its sodium salts are used. Individuals applying these products in residential setting should take appropriate precautions to avoid exposing children.

### 6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

The populations living in areas of California and other western states with boron-rich geological deposits have potentially high exposure to boron from drinking water and locally grown foods (Butterwick et al. 1989). Individuals using boron-containing cosmetics or medicines extensively, especially on damaged skin, may be exposed to higher-than-normal levels of boron (Beyer et al. 1983). Workers in industries producing or using boron-containing materials also have potentially high exposure as noted above (Section 6.5). People living in the vicinity of waste sites are also at risk of higher-than-normal exposure levels.

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**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 boron 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 boron.

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 summarizes many of the relevant physical and chemical properties of boron and selected boron compounds. There are adequate data for the physical and chemical properties of boron and boron compounds. No data needs are identified.

**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 2006, became available in May of 2008. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Current data on the production volume and uses of boron and boron compounds are available and no further production data are necessary at this time (Alam et al. 2003; USGS 2008, 2009); however, a data need exists for disposal methods of boron-containing wastes.

**Environmental Fate.** The only quantifiable mechanism that influences the fate of boron is soil adsorption (Rai et al. 1986). A data need exists for the adsorption and mobility of boron in soils low in aluminum oxide, since aluminum oxide content of soils is an important property of soil that will influence the mobility of boron (Bingham et al. 1971).

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**Bioavailability from Environmental Media.** Boron compounds can be absorbed following inhalation of contaminated workplace air, ingestion of contaminated food, or through damaged skin (Draize and Kelley 1959; Wong et al. 1964). The most significant routes of exposure near hazardous waste sites are likely to be through drinking boron-contaminated water and ingestion of locally grown food (Beyer et al. 1983; Butterwick et al. 1989). A data need exists for the amount of boron that is bioavailable from environmentally relevant media, such as drinking water, food, and soil.

**Food Chain Bioaccumulation.** Only one study was located where boron bioconcentration was actually measured (Tsui and McCart 1981). Future research may be helpful, but it appears that boron is not significantly bioconcentrated. There are no data on the biomagnification of boron in the food chain, but it is not likely that bioaccumulation is a major environmental concern. Therefore, there are no data needs at this time.

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

Data on boron levels in surface water and soil are available (Butterwick et al. 1989; Eckel and Langley 1988; EPA 1986b; Hall et al. 2004; Ordonez et al. 2003; Rope et al. 1988; USGS 1984). Data on boron concentration in drinking water are limited (Choi and Chen 1979; Davies 1990; McCabe et al. 1970; NIRS 1987; Waggott 1969). Boron concentrations in foods and beverages have been reported (Hunt et al. 1991; Minoia et al. 1994; Rainey et al. 1999, 2002). Additional data on boron concentrations in air and food, and more recent data on boron concentrations in drinking water would be useful in estimating the exposure of humans to boron.

**Exposure Levels in Humans.** Background levels of boron in human blood, urine, and hair have been reported (Alimonti et al. 1992; Culver et al. 1994a; Rosborg et al. 2003; Stokinger 1981). Additional data on blood and/or urine concentrations in individuals with potentially high exposure to boron would be useful in assessing the magnitude of human exposure.

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

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**Exposures of Children.** Children are exposed to boron by the same routes as adults. Rainey et al. (2002) reported daily boron intakes of 0.75 and 0.99 mg for infants aged 0–6 and 7–11 months respectively. In children, 0.86 and 0.80 mg daily boron intakes were reported for 1–3 and 4–8 year olds, respectively. In male adolescents, 0.90 and 1.02 mg were reported for 9–13 and 14–18 year olds, respectively. In female adolescents, 0.83 and 0.78 mg were reported for 9–13 and 14–18 year olds, respectively. Meacham and Hunt (1994) reported a daily intake of 0.333 mg for infants (6–11 months) from baby foods and beverages. There do not appear to be any childhood-specific means to decrease exposure to boron.

Boron intake from infant food was estimated to supply 47% of the 0.55 mg of daily boron to infants aged 6–11 months and toddlers aged 2 years 0.54 mg; 38% from fruits and juices and 19% from milk and cheese (Hunt and Meacham 2001). Children may also be exposed to boron by breastfeeding mothers. Boron has been detected in breast milk with concentrations ranging from 10 to 100 µg/L, although higher levels have been found in infant formulas (120 µg/L) and whole cow milk (280 µg/L) (Lopez-Garcia et al. 2009). Another study from St. John's, Newfoundland measured boron concentrations of lactating mothers' milk for full-term infants to be 30 and 28 µg/L at 1 and 12 weeks postpartum, respectively. In lactating mothers' milk for preterm infants boron concentrations were found to be 37 and 27 µg/L at 1 and 12 weeks, respectively (Hunt et al. 2004). The concentration of boron was determined in archived milk collected (1980–1984) from lactating mothers of full-term, exclusively breastfed infants living in Houston, Texas. The results indicated that infants were supplied average concentrations of 42±6.5 µg/L at 1 month old and 35±6.5 µg/L at 4 months old via breast milk (Hunt et al 2005). Hunt et al. (2004, 2005) indicated that boron concentrations over the first 4 months of lactating did not vary widely and were stable over time. The highest concentrations of boron detected in each study were 88 µg/L (Hunt et al. 2005) and 100 µg/L (Hunt et al. 2004).

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 boron were located. This substance is not currently one of the compounds for which a sub-registry has been established in the National Exposure Registry. The substance 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 this substance.

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**6.8.2 Ongoing Studies**

Ongoing studies pertaining to boron or boron compounds were identified in a search of the Federal Research in Progress database (FEDRIP 2009). A large comprehensive study on boron by C. Hunt at the United States Department of Agriculture in Grand Forks, North Dakota is collecting and analyzing dietary data and biochemical indices aimed at enhancing the quality of life through establishing mineral intakes, which support optimal bone health as well as general micronutrient roles in physiology and health.

D. Evans at Columbia University Health Sciences, New York, New York is sponsored by the Institute of Environmental Health Sciences to investigate the use of low-toxicity pesticides such as baits, gels, and boric acid. The USDA Water Management Research Unit in Parlier, California is attempting to develop strategies for sustainable agronomic systems for water reuse and bioremediation of soils impacted by the use of saline water containing high concentrations of boron and trace elements. B. Hoenisch at Columbia University is funded by the National Science Foundation to investigate validation of the boron/calcium proxy for surface seawater pH and application to measure anthropogenic ocean acidification (FEDRIP 2009).