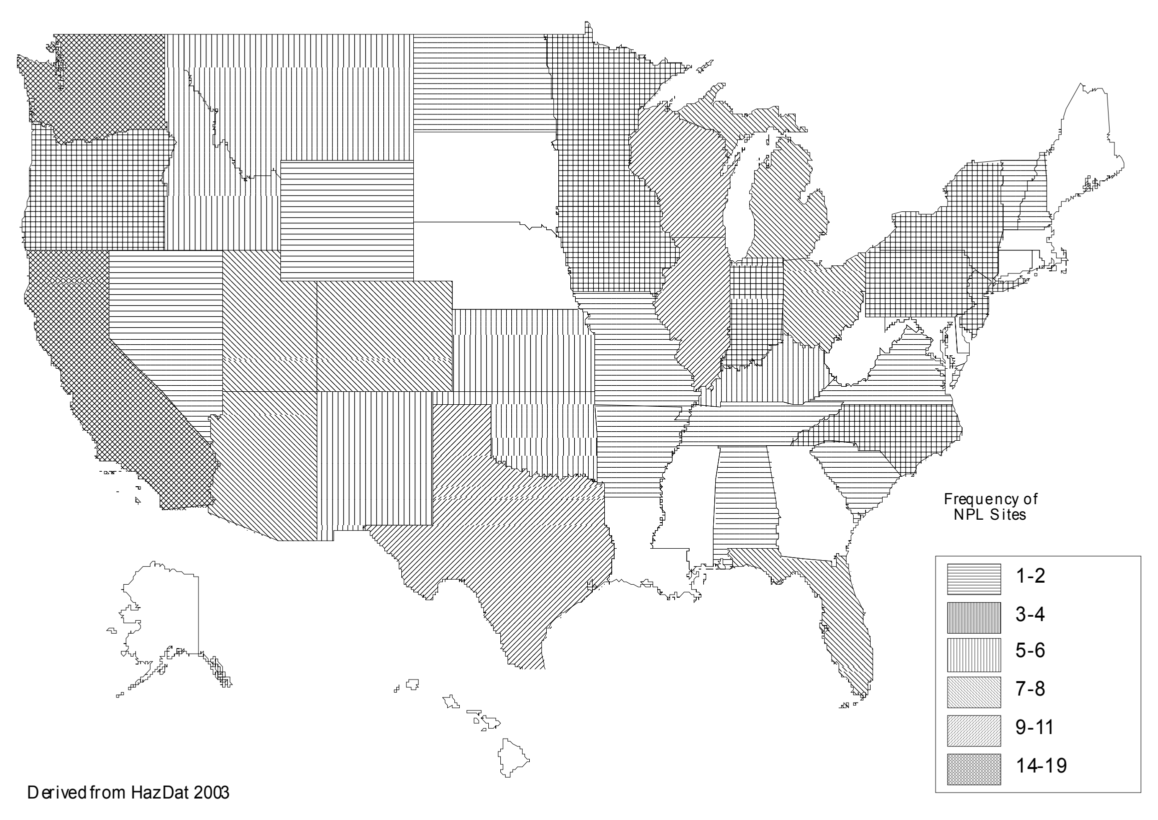
6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Fluorides, hydrogen fluoride, and fluorine have been identified in at least 188 of the 1,636 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2003). However, the number of sites evaluated for fluorides, hydrogen fluoride, and fluorine is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, all are located within the United States.

Fluorides are naturally-occurring components of rocks and soil and are also found in air, water, plants, and animals. They enter the atmosphere through volcanic emissions and the resuspension of soil by wind. Volcanoes also emit hydrogen fluoride and some fluorine gas. Fluorine is a highly reactive element and readily hydrolyzes to form hydrogen fluoride and oxygen. Hydrogen fluoride reacts with many materials both in the vapor phase and in aerosols. The resultant fluorides are typically nonvolatile, stable compounds. Marine aerosols also release small amounts of gaseous hydrogen fluoride and fluoride salts into the air (Friend 1989). Anthropogenic fluoride emissions include the combustion of fluorine-containing materials, which releases hydrogen fluoride, as well as particulate fluorides, into the air. Coal contains small amounts of fluorine, and coal-fired power plants constitute the largest source of anthropogenic hydrogen fluoride emissions. According to the Toxic Chemical Release Inventory (TRI), in 2001, the largest contributing industrial sectors were electrical utilities (TRI01 2003). Total air emissions of hydrogen fluoride by electrical utilities in 1998, 1999, 2000, and 2001 were reported as 64.1, 58.3, 58.3, and 55.8 million tons, respectively. Major sources of industrial fluoride emissions are aluminum production plants and phosphate fertilizer plants; both emit hydrogen fluoride and particulate fluorides (EPA 1998b). Other industries releasing hydrogen fluoride are: chemical production; steel; magnesium; and brick and structural clay products. Hydrogen fluoride would also be released by municipal incinerators as a consequence of the presence of fluoride-containing material in the waste stream. Hydrogen fluoride is one of the 189 chemicals listed as a hazardous air pollutant (HAP) in Title III, Section 112 of the Clean Air Act Amendments of 1990. Maximum achievable control technology (MACT) emission standards are being developed by the EPA for each HAP. The goal of

Figure 6-1. Frequency of NPL Sites with Fluoride, Hydrogen Fluoride, and Fluorine Contamination



Derived from HazDat 2003

HAP emissions control is to reduce human health risks (Kelly et al. 1994). In addition to industrial effluent and natural releases (e.g., weathering of rocks and runoff from soil), fluorides are released into surface water in municipal waste water as a result of water fluoridation.

In the atmosphere, gaseous hydrogen fluoride will be absorbed by atmospheric water (rain, clouds, fog, snow) forming an aerosol or fog of aqueous hydrofluoric acid. It will be removed from the atmosphere primarily by wet deposition. Particulate fluorides are similarly removed from the atmosphere and deposited on land or surface water by wet and dry deposition. Atmospheric precipitation weathers crustal rocks and soil, but dissolves out very little fluoride; most of the fluoride mobilized during weathering is bound to solids such as clays. Upon reaching bodies of water, fluorides gravitate to the sediment (Carpenter 1969). Fluorides have been shown to accumulate in some marine aquatic organisms (Hemens and Warwick 1972). When deposited on land, fluoride is strongly retained by soil, forming complexes with soil components. Fluorides in soils are transported to surface waters through leaching or runoff of particulate-bound fluorides. Leaching removes only a small amount of fluorides from soils. Fluorides may be taken up from soil and accumulate in plants. The amount of fluorides accumulated depends on the type of plant and soil and the concentration and form of fluoride in the soil. Fluorides may also be deposited on above-ground surfaces of the plant. Tea plants are particularly known to accumulate fluoride, 97% of which is accumulated in the leaves (Fung et al. 1999). Fluoride accumulates primarily in the skeletal tissues of terrestrial animals that consume fluoride-containing foliage. However, milk and edible tissue from animals fed high levels of fluorides do not appear to contain elevated fluoride concentrations (NAS 1971a).

In natural water, fluoride forms strong complexes with aluminum in water, and fluorine chemistry in water is largely regulated by aluminum concentration and pH (Skjelkvale 1994). Below pH 5, fluoride is almost entirely complexed with aluminum and consequently, the concentration of free F^- is low. As the pH increases, Al-OH complexes dominate over Al-F complexes and the free F^- levels increase. Fluoride forms stable complexes with calcium and magnesium, which are present in sea water. Calcium carbonate precipitation dominates the removal of dissolved fluoride from sea water (Carpenter 1969). Fluorine is incorporated into the calcium salt structure and removed from solution when the latter precipitates. Fluoride occurs in soil in a variety of minerals and complexes with aluminum, iron, and calcium. Fluorides occur predominantly as aluminum fluorosilicate complexes in acidic soils and calcium fluoride in alkaline soils. The availability of these soluble complexes increases with decreasing pH (Fung et al. 1999; Shacklette et al. 1974). This explains why acidic soils have both higher water-soluble fluoride and higher extractable aluminum levels. The retention of fluoride in alkaline soils depends largely upon the aluminum content of the soil.

The general population is exposed to fluoride through consumption of drinking water, foods, and dentifrices. Fluorides used in dentifrices are sodium fluoride, sodium monofluorophosphate, and stannous fluoride (Pader 1993). Populations living in areas with naturally high fluoride levels in water and soil may be exposed to high levels of fluoride in water. This is especially true if drinking water is derived from wells.

Fluoride intake in infants depends on whether or not the child is nursed. Fluoride intake by an infant who is exclusively breast fed is generally <2 μg/kg-day(Fomon and Ekstrand 1999). Levy et al. (2001) found that for most children, water fluoride intake was the predominant source of fluoride, especially through age 12 months. This was due in large part to children receiving fluoridated water mixed with infant formula concentrate (Levy et al. 1995b, 2001). Fluoride exposure was calculated to be 102, 105, and 167 μg/kg-day for infants consuming concentrated liquid milk-based formula, concentrated liquid isolated soy protein-based formula, and powdered milk-based formula, respectively, which were diluted with water that is 1 ppm in fluoride. Infants may be exposed to higher fluoride concentrations now than in the past. In the 1960s, nearly 80% of infants were fed cow's milk by 6 months of age. In 1991, 80% of 6-month-old infants were fed formula (Fomon and Ekstrand 1999).

Some plants, most notably tea, accumulate fluorides, and people who drink large quantities of tea may be exposed to high levels of fluoride in their diets. Populations living near industrial sources of fluoride may be exposed to higher levels of fluorides in the air they breathe. Vegetables and fruits grown near such sources may contain higher levels of fluorides particularly from fluoride-containing dust settling on the plant. Populations exposed to relatively high concentrations of fluoride include workers in fluoride-processing industries and individuals residing near such industries. Similarly, populations living near hazardous waste sites may also be exposed to high levels of fluoride by analogous routes.

6.2 RELEASES TO THE ENVIRONMENT

According to the TRI, in 2001, total releases of hydrogen fluoride to the environment (including air, water, soil, and underground injection) from 991 reporting facilities that produced, processed, or used hydrogen fluoride were 72.1 million pounds (TRI01 2003). Table 6-1 lists amounts released from these

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Hydrogen Fluoride

		Reported amounts released in pounds per year[a]						
State[b]	Number of facilities	Air[c]	Water	Underground injection	Land	Total on-site release[d]	Total off-site release[e]	Total on and off-site release
AK	2	73,027	No data	0	0	73,027	0	73,027
AL	28	3,304,387	0	0	12,000	3,316,387	18,596	3,334,983
AR	13	942,385	0	0	0	942,385	8	942,393
AZ	23	694,190	No data	0	3,405	697,595	1,062	698,657
CA	35	9,211	5	0	0	9,216	2,886	12,102
CO	17	795,831	No data	0	0	795,831	0	795,831
CT	5	107,388	0	0	0	107,388	10,732	118,120
DE	3	201,815	No data	0	0	201,815	0	201,815
FL	24	2,358,937	5	0	7,965	2,366,907	0	2,366,907
GA	28	3,286,300	0	0	0	3,286,300	2,944	3,289,244
IA	16	1,300,253	No data	0	0	1,300,253	0	1,300,253
ID	5	208,065	0	0	0	208,065	255	208,320
IL	41	2,255,380	1	0	5	2,255,386	1,510	2,256,896
IN	36	3,888,416	250	0	0	3,888,666	0	3,888,666
KS	16	775,771	0	0	0	775,771	930	776,701
KY	29	2,090,877	0	0	0	2,090,877	1,301	2,092,178
LA	19	613,860	250	0	11	614,121	0	614,121
MA	11	197,829	No data	0	0	197,829	237	198,066
MD	14	1,376,506	No data	0	0	1,376,506	15	1,376,521
ME	3	1,286	0	0	0	1,286	0	1,286
MI	27	2,139,731	0	0	0	2,139,731	39,376	2,179,107
MN	15	217,532	0	0	0	217,532	0	217,532
MO	29	2,464,416	0	0	158,300	2,622,716	0	2,622,716
MS	9	461,108	197	0	2,287	463,592	0	463,592
MT	7	167,298	0	0	0	167,298	0	167,298
NC	38	5,160,908	5	0	0	5,160,913	0	5,160,913
ND	8	490,133	0	0	0	490,133	260	490,393
NE	8	1,279,219	No data	0	0	1,279,219	0	1,279,219
NH	4	208,550	No data	0	0	208,550	391	208,941
NJ	15	249,406	0	0	0	249,406	2	249,408
NM	7	209,568	No data	0	0	209,568	420	209,988
NV	2	439,874	No data	0	0	439,874	0	439,874
NY	31	1,137,383	0	0	0	1,137,383	750	1,138,133
OH	64	6,147,565	1,601	4,400,000	0	10,549,166	34,884	10,584,050
OK	18	892,504	100	0	0	892,604	250	892,854
OR	21	67,943	0	0	18,398	86,341	0	86,341
PA	70	5,056,848	35	0	5	5,056,888	17,156	5,074,044

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Hydrogen Fluoride

		Reported amounts released in pounds per year[a]						
State[b]	Number of facilities	Air[c]	Water	Underground injection	Land	Total on-site release[d]	Total off-site release[e]	Total on and off-site release
PR	1	500	No data	0	0	500	0	500
RI	3	3,683	No data	0	0	3,683	0	3,683
SC	30	2,153,397	0	0	0	2,153,397	0	2,153,397
SD	2	89,000	No data	0	0	89,000	0	89,000
TN	19	2,069,004	0	0	0	2,069,004	0	2,069,004
TX	83	3,828,730	10	0	21	3,828,761	1,100	3,829,861
UT	14	467,778	0	0	24,930	492,708	0	492,708
VA	23	1,745,413	0	0	0	1,745,413	0	1,745,413
VT	2	4,141	0	0	0	4,141	0	4,141
WA	19	323,942	0	0	0	323,942	1,405	325,347
WI	24	1,231,556	0	0	0	1,231,556	0	1,231,556
WV	21	3,722,619	19,090	0	0	3,741,709	0	3,741,709
WY	9	337,011	No data	0	52,248	389,259	0	389,259
Total	991	67,248,474	21,549	4,400,000	279,575	71,949,598	136,470	72,086,068

Source: TRI01 2003

[a] Data in TRI are maximum amounts released by each facility.
[b] Post office state abbreviations are used.
[c] The sum of fugitive and stack releases are included in releases to air by a given facility.
[d] The sum of all releases of the chemical to air, land, water, and underground injection wells.
[e] Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

facilities grouped by state. In addition, 136,470 pounds of hydrogen fluoride were transferred off-site by these facilities (TRI01 2003). Starting in 1998, metal mining, coal mining, electric utilities and Resource Conservation and Recovery Act (RCRA)/solvent recovery industries were required to report to the TRI, industries with potentially large releases of hydrogen fluoride. The industrial sector producing, processing, or using hydrogen fluoride that contributed the greatest environmental releases was electrical utilities, which contributed 78% of the total environmental releases.

According to the TRI, in 2001, total releases of fluorine to the environment (including air, water, soil, and underground injection) from 9 reporting facilities that produced, processed, or used fluorine were 165,938 pounds (TRI01 2003). Table 6-2 lists amounts of fluorine released from these facilities grouped by state. The two largest contributing industrial sectors were electrical utilities and primary metals, which respectively contributed 65 and 19% of the total environmental releases. Neither sodium fluoride nor any other fluorides are listed on TRI. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Hydrogen fluoride is one of the 189 chemicals listed as a HAP in Title III, Section 112 of the Clean Air Act Amendments of 1990. MACT emission standards are being developed by the EPA for each HAP. The goal of HAP emissions control is to reduce human health risks (Kelly et al. 1994). The Final Air Toxic MACT Rule for fluoride emissions from primary aluminum reduction plants, published in 1997, was projected to reduce fluoride emissions by 3,700 tons per year. The Final Air Toxic MACT Rule for fluoride emissions from phosphoric acid manufacturing and phosphate fertilizer production, published in 1999, was projected to reduce fluoride emissions by 260 tons per year (EPA 2000).

Fluorides have been identified in a variety of environmental media (air, surface water, leachate, groundwater, soil, and sediment) collected at 188 of 1,636 current or former NPL hazardous waste sites (HazDat 2003).

6.2.1 Air

The major natural source of hydrogen fluoride emissions to the atmosphere is volcanoes. These emissions are estimated to range from 0.6 to 6 million metric tons per year. On average, <10% of these emissions are a result of large eruptions that are efficiently injected into the stratosphere (Symonds et al. 1988). Passive degassing of volcanoes is a major source of tropospheric hydrogen fluoride. In addition

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Fluorine

		Reported amounts released in pounds per year[a]						
State[b]	Number of facilities	Air[c]	Water	Under-ground injection	Land	Total on-site release[d]	Total off-site release[e]	Total on and off-site release
AL	1	0	31,328	0	0	31,328	0	31,328
IL	1	4,979	No data	0	0	4,979	0	4,979
KS	1	429	No data	0	107,282	107,711	0	107,711
LA	1	2,280	No data	0	0	2,280	0	2,280
OK	1	263	No data	0	0	263	0	263
PA	2	1,001	No data	0	0	1,001	0	1,001
PR	1	0	18,376	0	0	18,376	0	18,376
TX	1	0	No data	0	0	0	0	0
Total	9	8,952	49,704	0	107,282	165,938	0	165,938

Source: TRI01 2003

[a] Data in TRI are maximum amounts released by each facility.
[b] Post office state abbreviations are used.
[c] The sum of fugitive and stack releases are included in releases to air by a given facility.
[d] The sum of all releases of the chemical to air, land, water, and underground injection wells.
[e] Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

to hydrogen fluoride, volcanic gases also contain other fluorine compounds, namely SiF_4, H_2SiF_6, and F_2. Soil naturally contains fluoride, and resuspension of soil by wind also contributes to the atmospheric burden of fluorides in the form of soil minerals (NAS 1971a). Another source is sea salt aerosol, which releases small amounts of gaseous hydrogen fluoride and fluoride salts into the air. The marine aerosol is potentially a major source of tropospheric hydrogen fluoride (Friend 1989). However, these releases would be confined to the air over the oceans.

The largest anthropogenic source of hydrogen fluoride emissions to air in the United States is electrical utilities. Coal naturally contains fluorides as impurities and this will be released primarily in the form of hydrogen fluoride during combustion. Some of the fluoride in the coal may be absorbed onto fly ash or bottom ash. A typical 650 megawatt coal-burning power plant running at 67% capacity (the average for U.S. coal plants) would release 180,000 pounds of hydrogen fluoride per year (Rubin 1999). EPA (1998a) reports an emission factor of 0.15 pounds/ton (0.075 kg/Mg) for coal combustion under a variety of firing conditions. The Canadian Environmental Protection Act (CEPA) (1996) reports hydrogen fluoride emission factors for bituminous and lignite coals of 0.12 and 0.01 kg/Mg coal, respectively. Hydrogen fluoride is water soluble and emissions are readily controlled by acid gas scrubbers. Other gaseous fluorides that may occur in the flue gas are SiF_4 and H_2SiF_6. Emissions of fluorides from aluminum reduction processes are primarily gaseous hydrogen fluoride and particulate fluorides, principally aluminum fluoride and calcium fluoride. Emission factors for aluminum production are 0.03 pounds of total fluorides and 0.02 pounds of hydrogen fluoride per ton of aluminum produced (EPA 1998b). Fluorine-containing compounds are contained in the raw materials used to produce brick and structural clay products and, therefore, hydrogen fluoride and other fluoride compounds are emitted from kilns used to manufacture these products. In addition, coal may be used to fire the kilns and contribute to the fluoride emissions. In the production of phosphate fertilizers, gaseous fluorides (hydrogen fluoride and silicon tetrafluoride), as well as particulate fluorides, may be released. EPA's Office of Air Quality Planning and Standards has developed emission factors for hydrogen fluoride for these and other hydrogen fluoride emitting industries. Hydrogen fluoride would be released by municipal incinerators as a consequence of the presence of fluoride-containing material in the waste stream. The amount of hydrogen fluoride released in flue gas would depend on the fluorine content of the waste stream and the efficiency of pollution control devises used in the stack.

Anthropogenic hydrogen fluoride emissions to the atmosphere in Canada were estimated to be 5,400 metric tons per year, of which 75% was contributed by primary aluminum producers. Other industries releasing hydrogen fluoride in Canada and their relative contributions were: coal-burning utilities, 10%; chemical production, 6%; steel production, 4%; phosphate fertilizer production, 2%; and magnesium production, 1% (CEPA 1996).

On a global scale, emissions of fluorides from coal combustion and other anthropogenic sources are minor and of local concern compared with natural emissions, estimated as 2.5×10^{10} kg/year (Carpenter 1969). Anthropogenic releases of total fluorides into the atmosphere were 155,300 tons/year from the major fluoride-processing industries measured between 1964 and 1970 (EPA 1980a). The major contributors were steel, brick, tile, and aluminum manufacturing, combustion of coal, and production of phosphorus and phosphate fertilizer (EPA 1980a; NAS 1971a). In 1977 and 1978, monthly atmospheric emission factors for fluorides from the Kitimat aluminum plant in British Columbia, Canada ranged from 4.0 to 6.8 kg fluoride per ton of aluminum produced; production capacity was 300,000 tons of aluminum per year (Sauriol and Gauthier 1984). Subsequently, regulations were established that set emissions standards for aluminum manufacturing (EPA 1980b) and phosphate fertilizer plants (EPA 1975). Fluorides can also enter the atmosphere in dusts and aerosols from the manufacture and use of pesticides such as sodium fluoride, sodium fluorosilicate, barium fluorosilicate, and cryolite (NAS 1971a). In the United States, fluoride emissions from coal-burning electric utilities are estimated to be around 37×10^6 kg/year (Bauer and Andren 1985).

There is evidence that emissions of fluorides have been declining. Fluoride in precipitation has declined since 1967 (Ares 1990). A recent study from a forested area near Cologne, Germany registered a sharp decline in the fluoride content of Roe deer antlers from peak levels in the 1950s and 1960s (Kierdorf and Kierdorf 2000). In the 1990s, levels were almost an order of magnitude lower than the peak levels, which are attributed to reduced emissions from stationary sources. Fluoride is a skeletally-deposited contaminant, and it can be assumed that fluoride is mobilized during the annual antler growth period and transported to the mineralizing antlers. Therefore, the fluorine content of antlers is a good indicator of fluoride release.

According to the TRI, in 2001, releases of 67.2 million pounds of hydrogen fluoride to air from 991 reporting facilities accounted for 93% of the total environmental releases of hydrogen fluoride (TRI01 2003). Table 6-1 lists amounts of hydrogen fluoride released to air from these facilities grouped by state. The industrial sector contributing the largest release of hydrogen fluoride to air was electrical utilities, which contributed 83% of releases to air.

According to the TRI, in 2001, releases of 8,952 pounds of fluorine to air from 9 reporting facilities accounted for 5% of the total environmental releases of fluorine (TRI01 2003). Table 6-2 lists amounts of fluorine released to air from these facilities grouped by state. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list.

According to the TRI, total air emissions for hydrogen fluoride ranged from 15.9 million pounds in 1998 to 8.9 million pounds in 1994, during the period from 1988 to 2001. Total air emissions of fluorine have decreased from 18,319 pounds in 1995 to 8,523 pounds in 2001 (TRI01 2003). This trend information only includes emission data from the original industry subtotal, those industries with Standard Industrial Classification (SIC) Codes 20–39. Starting in 1998, metal mining, coal mining, electric utilities, Resource Conservation and Recovery Act (RCRA)/solvent recovery industries, and chemical wholesalers were also required to report. Of these industries, electrical utilities contribute significantly to emissions of hydrogen fluoride to air. Total air emissions of hydrogen fluoride by electrical utilities in 1998, 1999, 2000, and 2001 were reported as 64.1, 58.3, 58.3, and 55.8 million tons, respectively.

Fluorides were detected in the air at 8 of the 188 current or former NPL hazardous waste sites, where they were detected in some environmental media (HazDat 2003).

6.2.2 Water

Natural sources of fluoride released to waters are primarily a result of runoff from the weathering of fluoride-containing rocks and soils and the leaching of fluorides from the soil into groundwater. In the western regions of the United States, rocks and soils have greater than average concentrations of fluoride; as a result, greater amounts of fluorides leach into the groundwater. Leaching from alkaline igneous rocks, dolomite, phosphorite, and volcanic glasses may result in water with high-fluoride levels (EPA 1980a; NAS 1971a).

Anthropogenic sources contributing to fluoride levels in water include atmospheric deposition of emissions from coal-fired power plants and other industrial sources that are deposited directly into water or that are first deposited on land and enter waterways in runoff. Most of this deposition is in the form of precipitation. Waste water may enter surface water directly or as effluent of water treatment plants. Since much of the nation's water supplies are fluoridated to a level of 0.7–1.2 ppm to decrease the incidence of tooth decay (DHHS 1991), this will contribute to fluoride in effluents from treatment plants.

According to the TRI, in 2001, releases of 21,549 pounds of hydrogen fluoride to water from 991 reporting facilities accounted for 0.030% of the total environmental releases of these substances (TRI01 2003). Table 6-1 lists amounts of hydrogen fluoride released to water from these facilities grouped by state. According to the TRI, in 2001, releases of 49,704 pounds of fluorine to water from 9 reporting facilities accounted for 30% of the total environmental releases of this substance (TRI01 2003). Table 6-2 lists amounts of fluorine released to water from these facilities grouped by state. As of 1998, TRI no longer separately collects data on substances released indirectly to POTWs, part of which may ultimately be released to surface waters. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list.

Fluorides were detected in groundwater and surface water at 135 and 53 sites, respectively, of the 188 NPL hazardous waste sites where they were detected in some environmental media (HazDat 2003).

6.2.3 Soil

Fluoride comprises about 0.09% of the earth's crust, ranking 13th in order of abundance (Lindahl and Mahmood 1994). Fluoride-containing minerals include biotite, muscovite, hornblende, apatite, and fluorspar (NAS 1971a). Fluorides are released to soils from the weathering of crustal rock and minerals, deposition of fluorides released to air from natural and anthropogenic sources, and plant and animal residues. Man-made sources applied directly to soil include phosphate fertilizers, mine tailings, and landfilled industrial and municipal waste (EPA 1980a; NAS 1971a). In a study by Oelschläger (1971), fertilization with superphosphates added 8–20 kg fluoride/hectare to the soil. Soil contamination by atmospheric fluorides near an industrial source reflected the gradient of fluoride deposition. In one study, the total fluoride concentration was found to decrease over a distance of 8.8 km from 2,700 to 616 μg/g fluoride and the water extractable fraction decreased from 292 to 10 μg fluoride/g (Polomski et al. 1982).

According to the TRI, in 2001, releases of 279,575 pounds and 4.4 million pounds of hydrogen fluoride respectively to land and underground injection from 991 reporting facilities accounted for respectively 0.38 and 6.1% of total environmental releases of these substances (TRI01 2003). Table 6-1 lists amounts of hydrogen fluoride released to land and underground injection from these facilities grouped by state. According to the TRI, in 2001, 107,282 pounds of fluorine were released to land from 9 reporting facilities accounted for 65% of the total environmental releases of this substance (TRI01 2003). However, it is not clear how a gaseous substance can be released to land, and this figure is likely an error. Table 6-2 lists amounts of fluorine released to air from these facilities grouped by state. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list.

Fluorides were detected in soil and sediment collected at 32 and 22 sites, respectively, of the 178 NPL hazardous waste sites, where they were detected in some environmental media (HazDat 2003).

6.3 ENVIRONMENTAL FATE

6.3.1 Transport and Partitioning

In the atmosphere, gaseous hydrogen fluoride will be absorbed by atmospheric water (rain, clouds, fog, snow) forming an aerosol or fog of aqueous hydrofluoric acid. It will be removed from the atmosphere primarily by wet deposition (including rainout or in-cloud scavenging and washout or below-cloud scavenging). Particulate fluorides are similarly removed from the atmosphere and deposited on land or surface water by wet and dry deposition. Atmospheric precipitation weathers crustal rocks and soil, but dissolves out very little fluoride; most of the fluoride mobilized during weathering is bound to solids such as clays. Upon reaching bodies of water, fluorides gravitate to the sediment (Carpenter 1969).

Most of the fluorides in the oceans are received from rivers; a lesser amount comes from atmospheric deposition. Losses occur in aerosols to the atmosphere and incorporation into the tissue of aquatic organisms. Fluorides have been shown to accumulate in some marine aquatic organisms. In a study by Hemens and Warwick (1972), toxic effects due to fluorosis were observed in species of mussel, mullet, crab, and shrimp in an estuary where waste from an aluminum plant was released.

Fluoride is strongly retained by soil, forming complexes with soil components. Fluorides in soils are transported to surface waters through leaching or runoff of particulate-bound fluorides. Leaching removes only a small amount of fluorides from soils. Oelschläger (1971) reported that about 0.5–6.0% of the yearly increment of fluoride added to forest and agricultural areas through the application of phosphate fertilizer was lost in the leaching process. In this study, superphosphates added 8–20 kg fluoride/hectare to the soil, while seepage water contained between 52 and 208 μg fluoride/L, depending upon soil levels of clay, lime, and fluoride.

Fluorides may be taken up from soil and accumulate in plants. They may also be deposited on above-ground surfaces of the plant. Tea plants are known to accumulate fluoride, 97% of which is accumulated in the leaves and 3% in the other parts of the plant. Fung et al. (1999) observed that the fluoride contents of tea leaves were 1,000 times the soluble fluoride content of the soil and 2–7 times the total fluoride content. The amount of fluoride taken up by plants is more a function of the soil type, its pH, and calcium and phosphorous content than of the total fluoride content of the soil (Brewer 1966). The addition of soluble fluoride to unlimed soil will result in increased fluoride uptake. In studies of plants grown on heavily polluted soil near aluminum smelters, uptake was via the roots and the stomata. Fluoride concentrations were much lower in the leaves than in the roots of plants, and most of the fluoride adsorbed by the roots was desorbed in water. Others have found that fluoride uptake is increased by the presence of aluminum, probably due to the uptake of aluminum–fluoride complexes. The fluoride uptake in ryegrass and clover from contaminated soil was strongly correlated with water and calcium chloride-extractable fluoride in the soil (Arnesen 1997). In this study, the fluoride content of pasture ryegrass exceeded the recommended fluoride limit only in grass grown in the most polluted soil, while that in clover exceeded this limit even in moderately polluted soil.

Fluoride accumulates primarily in the skeletal tissues of terrestrial animals that consume fluoride-containing foliage. However, milk and edible tissue from animals fed high levels of fluorides do not appear to contain elevated fluoride concentrations (NAS 1971a). Fluoride is taken up by hens and concentrated in the shell of their eggs. Hens living in the vicinity of two major coal-fired power plants had fluoride levels in egg shells of 1.75 mg/kg compared with reference means of 0.07 mg/kg, indicating significant uptake of anthropogenic fluoride (de Moraes Flores and Martins 1997).

6.3.2 Transformation and Degradation

6.3.2.1 Air

Hydrogen fluoride is the most abundant gaseous fluoride released into the atmosphere. It reacts with many materials both in vapor and in aerosols. For example, hydrogen fluoride reacts with silica, forming silicon tetrafluoride. However, no information was found on the reactions of hydrogen fluoride with common atmospheric species or estimates of its overall atmospheric half-life. The predominant mode of degradation of inorganic fluorides in the air is hydrolysis. Silicon tetrafluoride, a major industrial pollutant, reacts with water vapor in air to form hydrated silica and fluorosilicic acid. Sulfur hexafluoride, a gaseous dielectric for electrical and electronic equipment, reacts with water at elevated temperatures (>850 °C) to form sulfuric acid and hydrogen fluoride (Guo et al. 2001). Molecular fluorine hydrolyzes to form hydrogen fluoride and oxygen. Hydrolysis of uranium hexafluoride, which is used in nuclear power applications, also produces hydrogen fluoride as well as nonvolatile uranyl fluoride. These compounds are then removed from the atmosphere by condensation or nucleation processes (NAS 1971a). Fluorides emitted by industries in particulate matter are stable compounds that do not readily hydrolyze.

6.3.2.2 Water

Contrary to traditional thought, hydrogen fluoride, a very weak acid in dilute solution, is dissociated in solution, but forms tight ion pairs $F^{-}...H^{+}–OH_2$, unique to F^-, which reduce the thermodynamic activity coefficient of H_3O^+ (Cotton et al. 1999). In natural water, fluoride ions form strong complexes with aluminum, and fluorine chemistry in water is largely regulated by aluminum concentration and pH. Below pH 5, fluorine is almost entirely complexed with aluminum and consequently, the concentration of free F^- is low. As the pH increases, Al-OH complexes dominate over Al-F complexes and the free F^- level increases. The dominant Al-F complex at pH <5 is AlF^{2+} (Skjelkvale 1994). In the absence of aluminum, dissolved fluorides are usually present as free F^- at neutral pH (Bell et al. 1970). As the pH decreases, the proportion of F^- decreases, while HF_2^- and undissociated hydrogen fluoride increase. Levels of undissociated hydrogen fluoride also increase in concentrated solutions. Fluorine can form stable complexes with calcium and magnesium, which are present in sea water. Using the stability constants valid for sea water, 51.0% of fluorine will be present as free F^-, 47.0% as MgF^+, and 2.0% as CaF^+ (Stumm and Morgan 1981). Calcium carbonate precipitation dominates the removal of dissolved fluoride from sea water. Fluoride is incorporated into the calcium salt structure and is removed from solution when the latter precipitates. The next most important removal mechanism is incorporation into calcium phosphates (Carpenter 1969). The residence time of dissolved fluoride in the oceans, as calculated from its sedimentation rate, is 2–3 million years (Carpenter 1969).

In a recent review article, different models of the equilibria of the hexafluorosilicate anion in water solution were compared. It was concluded that concentrations of any fluorosilicate species are extremely small at drinking water pH (Urbansky 2002). The analysis presented reaffirms the conclusions made earlier by Feldman et al. (1957), that in drinking water with a pH of ≥5, fluoridated with sodium silicofluoride to a concentration of ≤16 ppm of fluoride ion or less, silicofluoride is completely hydrolyzed to silicic acid, fluoride ion, and hydrogen fluoride. While the kinetics of dissociation and hydrolysis of the hexafluorosilicate anion are not well understood from a mechanistic or fundamental perspective, the rate data suggest that equilibrium should be achieved by the time drinking water reaches the consumer (Urbansky 2002).

6.3.2.3 Sediment and Soil

Fluoride occurs in soil as a variety of minerals and complexes with aluminum, iron, and calcium. At low pH, aluminum complexes, AlF_3, AlF_2^+, and AlF^{2+}, are the dominant dissolved species, and the availability of these soluble complexes increases with decreasing pH (Fung et al. 1999; Shacklette et al. 1974). This explains why more acidic soils have both higher water-soluble fluoride and higher extractable aluminum levels. While aluminum may complex with organic ligands, this does not appear to alter aluminum-fluoride complexation significantly (Ares 1990). In certain soils in which calcium is present mostly as calcium fluoride and in which there is sufficient alumina, fluoride is fixed by the formation of relatively insoluble aluminum fluorosilicate, $Al_2(SiF_6)_3$ (Brewer 1966).

6.3.2.4 Other Media

Several species of plants have the capacity to convert fluoride obtained from soil or water into carbon-fluorine compounds such as monofluoroacetic acid, ω-fluoro-oleic acid, ω-fluoropalmitic acid, and ω-fluoromyristic acid (Marais 1944; NRC Canada 1971; Ward et al. 1964). These compounds have a higher mammalian toxicity than inorganic fluoride salts.

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

6.4.1 Air

The concentration of fluoride in ambient air depends on the presence of industrial sources of fluoride in the area, the distance from the sources, meteorological conditions, and topography (Davis 1972). Ambient concentrations of hydrogen fluoride measured in the United States (ca. 1985) ranged from 1.0 to 7.5 $\mu g/m^3$ (Kelly et al. 1993). In a study by Thompson et al. (1971) of 9,175 urban air samples in the United States in 1966, 1967, and 1968, 87% of all measurements at urban stations and 97% of all measurements at non-urban stations showed fluoride concentrations below 0.05 $\mu g/m^3$, the threshold of detectability. Only 18 measurements (0.2%) exceeded 1.00 $\mu g/m^3$; the maximum concentration was 1.89 $\mu g/m^3$ at urban locations and 0.16 $\mu g/m^3$ at non-urban locations (Yunghans and McMullen 1970).

The ambient air concentration of gaseous fluoride varies from 0.01 to 1.65 μg/m^3 in Canada and the United States, approximately 75% of which exists as hydrogen fluoride (CEPA 1996).

Atmospheric hydrogen fluoride concentrations were measured at nine sites in Southern California during the last 8 months of 1986. Samples were collected every 6th day for a 24-hour sampling period. Average hydrogen fluoride concentrations ranged between 0.13 μg/m^3 (0.15 ppb) and 0.22 μg/m^3 (0.25 ppb) (Hance et al. 1997). The lowest concentration was at a remote off-shore location (San Nicolas Island). The maximum hydrogen fluoride levels at the eight on-shore sites varied from 0.34 μg/m^3 (0.38 ppb) to 1.91 μg/m^3 (2.14 ppb). Ambient hydrogen fluoride levels were fairly constant throughout the year. However, there were occasional isolated peaks in the hydrogen fluoride levels. These are thought to be the result of accidental releases. Although there are major refineries and chemical plants in the area that use hydrogen fluoride, it was not possible to correlate the spike in hydrogen fluoride levels with any reported accidental releases.

Atmospheric fluoride levels are often elevated near fluorine-related industrial operations. A 1976 study reported fluoride levels 1.5 km from an aluminum plant that emitted 34 kg fluoride/hour (Krook and Maylin 1979). The average particulate fluoride level was 0.31 μg/m^3 (5.53 μg/m^3, 12-hour maximum), and the average gaseous fluoride level was 0.36 μg/m^3 (6.41 μg/m^3, 12-hour maximum). An indicator of atmospheric fluoride levels is the amount of fluoride dust deposited on foliage. After an aluminum plant began operating in 1958 in Oregon, the average fluoride content of foliage in cherry and peach trees jumped from 13 to 65 and 76 ppm, respectively. The highest average values occurred 2 years later, measuring 196 and 186 ppm, respectively (NAS 1971a). Since then, the fluoride levels in foliage dropped appreciably.

6.4.2 Water

Surface Water. Fluoride levels in water vary according to local geology and proximity to emission sources. In rivers, fluoride concentrations range from <1 to 6,500 μg/L; the average fluoride concentration is around 200 μg/L (Fleischer et al. 1974). Fluoride levels may be higher in lakes, especially in saline lakes and lakes in closed basins in areas of high evaporation. The Great Salt Lake in Utah has a fluoride content of 14,000 μg/L (Fleischer et al. 1974). Lakes in East Africa where fluoride leaches from the alkalic rocks in the region contain 1,000–1,600 mg/L of fluoride. Fluoride levels in the Norwegian ‘1,000 lake survey’ ranged from <5 to 560 μg/L with one outlier at 4,120 μg/L and a median of 37 μg/L (Skjelkvale 1994). The highest levels were found in lakes in Southern Norway that receive the greatest amounts of acid rain. Fluoride concentrations at these lakes are correlated with sulfate concentrations, an indicator of acid rain. In studies of natural water in the Rift Valley of Kenya and Tanzania, high fluoride levels in water and a high incidence of fluorosis were correlated with low levels of calcium and magnesium in the water (Gaciri and Davies 1993). Calcium carbonate entraps fluorides and removes it from solution. These results are consistent with researchers who maintain that waters low in hardness and high in alkalinity present the highest risk of fluorosis. Other reasons for high fluoride levels in some Kenyan waters are evaporative concentration resulting in much higher fluoride levels in surface water than groundwater, fluoride-rich volcanic rocks in the region, and contamination by waste water from fluorspar mining. Seawater contains more fluoride than fresh water, approximately 1,200–1,500 μg/L (Bowen 1966; Carpenter 1969; Fleischer et al. 1974; Goldschmidt 1954).

Fluoride content of waters for Yellowstone National Park ranged from 0.5 mg/L in Yellowstone River to 24.0 mg/L in the Midway Geyser Basin. Fluoride concentrations in some selected thermal waters in Idaho ranged from 9 to 30 mg/L. Data from more than 300 geothermal waters in the Western United States indicate that at least 68% of these waters contain fluoride, with concentrations ranging from 2.1 to 30 mg/L. Fluoride concentrations from a regular well and a geothermal well from a ranch in Idaho were 0.8 and 14.2 mg/L, respectively. Use of geothermal well water for irrigation induces high fluoride levels in alfalfa and pasture grasses consumed by cattle (Miller et al. 1999).

Groundwater. The fluoride content of groundwater generally ranges from 20 to 1,500 μg/L (EPA 1980a; Fleischer 1962). Fleischer et al. (1974) contains a map of the fluoride content in groundwater in the conterminous United States by county. Highest fluoride levels in groundwater are generally found in the southwest, and maximum groundwater levels in Nevada, southern California, Utah, New Mexico, and western Texas exceed 1,500 μg/L. In a survey of fluoride levels in Texas groundwater in which water from nearly 7,000 wells in 237 counties were analyzed, Hudak (1999) identified four regions with high fluoride levels. In one region in northwest Texas, at least 50% of the wells sampled in each of five counties had fluoride levels exceeding the primary drinking water standard of 4,000 μg/L. County-median fluoride concentrations ranged from 90 to 5,110 μg/L. Twenty-five counties had median fluoride levels above the secondary standard of 2,000 μg/L and 84 counties had median concentrations higher than 1,000 μg/L, the target fluoride concentration for many water fluoridation programs. Factors responsible for the elevated fluoride levels were the mineral constitution of the aquifers, seepage from nearby saline formations, and low recharge and dilution rates in the aquifers. The results of this study suggest that geology has an important influence on the distribution of fluoride in Texas groundwater. Groundwater constitutes approximately 60% of the water consumed in Texas.

Fluoride levels in groundwater are higher than in surface water because they are more influenced by the rocks in which they occur (EPA 1980a; Fleischer et al. 1974; NAS 1971a; WHO 1984). Groundwater from granitic rock, basaltic rock, limestones and dolomites, and shales and clays average 1,200, 100, 300, and 400 μg fluoride/L, respectively, while groundwater from alkalic rocks average 8,700 μg fluoride/L (Fleischer et al. 1974). An example of the influence of geology on the concentration of fluorides in groundwater is illustrated by a region in the Pampa in Argentina where groundwater is alkaline and moderately saline (Nicolli et al. 1989). Forty-two percent of groundwater samples from this area had fluoride levels exceeding 1,400 μg/L and the maximum level was 6,300 μg/L. The highest levels of fluoride were found in waters with the highest sodium and potassium contents.

Drinking Water. The concentration of fluoride in 384 Norwegian waterworks sampled during the winter of 1983 ranged from 13 to 1,210 μg/L with a mean and median of 87 and 58 μg/L, respectively (Flaten 1991). Fluoride is a naturally-occurring constituent of groundwater and the fluoride in the water was mostly a consequence of local soil or rock formations. In addition, there was evidence that the fluoride levels were influenced by local sources and long-range transport. In a random survey of farmstead wells by the Kansas Department of Health and Environment, 2 of the 103 wells sampled contained fluoride levels above EPA's maximum contaminant level (MCL) that was reported at the time as 1,800 μg/L for public water supplies (Steichen et al. 1988). The highest fluoride level found in this study was 2,300 μg/L.

Rain Water. Rain water sampling was conducted in eight arctic catchments in Northern Europe from May to September in 1994 (Reimann et al. 1997). Some of the world's largest industrial sources are in this region. The median concentrations of fluoride in all of the 30-day composite rain water samples from the eight catchments were <0.05 mg/L. In five of the catchments, all samples contained <0.05 mg/L of fluoride. The maximum concentration of fluoride was 1.53 mg/L. Concentrations of fluoride in precipitation in Norway ranged from 0 to 253 μg/L with volume-weighted averages from 13 to 25 μg/L (Skjelkvale 1994). Correlations of fluoride content with other ions indicated that the fluoride is not of marine origin and is mostly correlated with industrial sources of sulfur oxides. Higher fluoride levels in some rain samples were due to nearby aluminum smelters.

6.4.3 Sediment and Soil

Fluorides are widely distributed in the earth's crust. The concentration of fluoride in soils and other surficial materials in the conterminous United States ranges from <10 to 3,700 ppm with a mean of 430 ppm (Shacklette and Boerngen 1984). Other values for the mean fluoride content of mineral soils ranges from 200 to 300 ppm (Bowen 1966; NAS 1971a; Worl et al. 1973). The fluoride content of organic soils is usually lower. The chief fluorine-containing minerals are fluorspar, cryolite, and fluorapatite. In soils with high concentrations of these minerals, the soil fluoride content is much higher and may range from 7 to 38 g/kg (Smith and Hodge 1979). In most soils, fluorine is associated with micas and other clay minerals. Robinson and Edgington (1946) reported the fluorine content of 137 soil samples in 30 soil profiles as ranging from trace to 7.07% fluorine, with an average of 0.029%. While the highest fluoride concentration was found in a Tennessee soil high in rock phosphate (apatite), the main source of fluoride in the soil were micaceous clays. In general, silt and clay loam soils had higher fluoride content than sandy soils. Average fluoride soil concentrations differ between the eastern and western United States. The average concentrations are 340 ppm in the east and 410 ppm in the west (EPA 1980a). Fluoride concentrations also tend to increase with soil depth. Of 30 domestic soil samples, the mean fluoride concentration at a depth of 0–3 inches was 190 ppm, whereas the mean concentration at a depth of 3–12 inches averaged 292 ppm (NAS 1971a).

The fluoride content of soil may be increased by the addition of fluoride-containing phosphate fertilizers (WHO 1984). Soils near industrialized sources show elevated concentrations that decrease with distance from the source and depth below the surface. Concentrations of fluoride in the top 0.5 inches of soil located near a phosphorus extraction facility near Silver Bow, Montana, were reported to range from 265 to 1,840 ppm (Van Hook 1974). Humus near an elementary phosphorus plant in Newfoundland, Canada, where 80–95% of balsam fir trees were dead because of the pollution, contained average fluoride levels of 58 ppm dry weight in 1973 and 24.2 ppm in 1974 (Sauriol and Gautier 1984). In 1975, when the plant was not in operation during the growing season, the humus fluoride content was 8.1 ppm. Humus fluoride levels in an uncontaminated zone were 2.0 ppm.

The fluoride concentrations in recent oceanic sediments appear to vary between 450 and 1,100 ppm (Carpenter 1969). Similar levels have been reported for fresh water lakes.

6.4.4 Other Environmental Media

Several factors influence the level of fluorides in food. These include the locality in which the food is grown and whether there were sources of fluoride emissions in the area, the amount of fertilizer and pesticides applied, the type of processing the food receives, and whether fluoridated water is used in food preparation (McClure 1949; Myers 1978; Waldbott 1963b). Foods characteristically high in fluoride content are certain types of fish and seafood (1.9–28.5 mg/kg), especially those types in which the bones are consumed, bone products such as bone meal and gelatin, and tea, which contains approximately 0.52 mg fluoride/cup (Cook 1969; Kumpulainen and Koivistoinen 1977).

During a comprehensive total diet study, foods were collected in Winnipeg, Canada in 1987 and were processed into 148 composite food samples (Dabeka and McKenzie 1995). The mean, median, and range of fluoride in all samples were 325, 99, and <11–4,970 ng/g, respectively. Food categories with the highest mean fluoride levels were fish (2,118 ng/g), beverages (1,148 ng/g), and soups (606 ng/g). Individual samples with the highest fluoride levels were tea (4,970 ng/g), canned fish (4,570 ng/g), shellfish (3,360 ng/g), cooked veal (1,230 ng/g), and cooked wheat cereal (1,020 ng/g). The drinking water used to prepare the food came from a single source containing the optimal fluoride concentration of 1 mg/L. This fluoride would contribute substantially to the fluoride levels in the food. The fluoride level in 68 samples of cows' milk purchased in retail stores throughout Canada ranged from 7 to 86 ng/g, with a mean and median concentration of 41 and 40 ng/g, respectively (Dabeka and McKenzie 1987). Provincial mean levels varied from 25 to 74 ng/g. Other studies of fluoride levels in cows from uncontaminated areas reported similar fluoride levels in milk (Dabeka and McKenzie 1987). A study compared fluoride content in foods and beverages from a negligibly fluoridated community (Connersville, Indiana) and an optimally fluoridated community (Richmond, Indiana). The fluoride concentrations in Connersville and Richmond are 0.16±0.01 and 0.90±0.05 μg F/g. It was found that fluoride content in non-cooked and non-reconstituted foods and beverages ranged from 0.12 to 0.55 μg F/g and that there was no significant difference between the two communities. The difference in fluoride content of foods prepared and/or cooked with water from the two study sites were statistically different, except in the case of cooked vegetables (Jackson et al. 2002).

Beverages may contain fluoride from the fluoride content of the water used in their production, as well as the base ingredients (e.g., fruit, flavoring) in the product. In a North Carolina study, beverages purchased from six regions of the state showed considerable differences in the fluoride content of the product. This was especially true for carbonated beverages. The ranges (means) of fluoride concentrations in various beverage types were: sodas, 0.07–1.37 ppm (0.28 ppm); juices, 0.01–1.70 ppm (0.36 ppm); punches, 0.00–1.44 ppm (0.33 ppm); tea, 0.61–6.68 ppm (2.56 ppm); and Gatorade, 0.02–1.04 ppm (0.85 ppm) (Pang et al. 1992). Fluoride concentrations were measured in 332 carbonated soft drinks, manufactured by 10 companies, which are available in Iowa grocery stores. Fluoride concentrations were found to range from 0.02 to 1.28 ppm, with a mean of 0.72 ppm. For 71% of the drinks analyzed, fluoride concentrations exceeded 0.60 ppm. Concentrations were found to vary substantially by production site, even within the same company and for the same product (Heilman et al. 1999).

The fluoride content of most plant foliage growing in areas removed from sources of fluoride pollution ranges from 2 to 20 ppm dry weight (Brewer 1966). A notable exception is tea plants. The highest fluoride concentration reported in vegetation was over 8,000 ppm in tea leaves. Tea plants take up fluoride from soil and accumulate it in the leaves. A large percentage of the total fluoride, 25–84%, is released during infusion, and tea is considered to be a major source of fluoride. The older tea leaves contain more fluoride and brick tea, which is prepared from older leaves, may be very high in fluoride content, 4.73–7.34 mg/L, compared with quality green and black tea, which is prepared from younger leaves and may contain 1.2–1.7 and 0.9–1.9 mg/L, respectively (Fung et al. 1999).

Fruits and vegetables grown in industrial areas where fluoride emissions are high contain elevated fluoride levels compared with those grown in control areas. The highest levels are found in the leafy parts of the plants rather than the roots. In a Polish study, vegetables grown 1.5 and 5 km from a steel plant contained average fluoride levels of 0.54–8.82 and 0.39–4.95 mg/kg, respectively, compared with 0.02–0.41 mg/kg for controls (Krelowska-Kulas 1994). Fruits grown 1.5 and 5 km from the steel plant contained average fluoride levels of 1.42–5.44 and 1.24–2.75 mg/kg, respectively, compared with 0.40–1.05 mg/kg for controls. Vegetables from the Saint-Régis Mohawk Indian reservation contained an average of 1.54–45.17 ppm fluoride dry weight compared with 0.63–11.3 ppm fluoride for vegetables from an uncontaminated site (Sauriol and Gauthier 1984). The reservation is located along the St. Lawrence River, straddling territory in New York State, Québec, and Ontario, where there are three potential sources of industrial fluoride emissions, namely two aluminum plants and a phosphate fertilizer plant.

Fluoride concentrations in vegetation form Yellowstone National Park varies over a wide range from 3 to 430 ppm. Studies where plants were watered by spray treatments containing 4 ppm fluoride showed that plants accumulated up to 36 ppm fluoride (dry weight), but a significant amount of this could be removed by washing the leaves in distilled water. In another experiment using 6 ppm fluoride solution, leaf analysis contained up to 55 ppm fluoride in the unwashed leaves and 35 ppm in washed leaves. Fluoride content in vegetation around a phosphate plant was found to range from 4 to 718 ppm. Fluoride was present in the air in the form of particulate fluorides and hydrogen fluoride gas (Miller et al. 1999).

Fluoride levels in various marine crustaceans were found to range from not detected to 2,500 (whole-body), not detected to 5,977 (exoskeleton), and not detected to 257 (muscle) μg/g, dry weight. Fluoride levels in saltwater fish were found to range from 45 to 1,207 (skeletal bone) and from 1.3 to 26 (muscle) mg/kg, wet weight (Camargo 2003).

The fluoride concentration in most dental products available in the United States ranges from 230 ppm (0.05% NaF mouth rinse) to 12,300 ppm (1.23% acidulated phosphate fluoride gel) (NRC 1993). The most commonly used dental products, toothpastes, contain 900–1,100 ppm fluoride (ca. 0.10%), most often as sodium fluoride, but also as disodium monofluorophosphate.

The fluoride concentration of a bituminous coal used in power generation is around 65.0 ppm dry weight and may contain up to 200 mg fluoride/kg (Rubin 1999; Skjelkvale 1994). The fluoride in the coal occurs predominantly as fluorapatite and fluorspar. Hydrogen fluoride and other fluorides are released from the coal during combustion. Bauer and Andren (1985) studied fluoride emissions from an electricity-generating plant in Portage, Wisconsin that consisted of two nearly-identical 527-MW pulverized-coal units, differing only in the type of coal burned and the operating conditions. In one unit, emissions contained a median of 1.9 mg fluoride/scm (86% of available fluoride in coal) and the other contained a median of 0.22 mg fluoride/scm (4.2% of available fluoride in coal). The first unit burned a bituminous coal from Colstrip, Montana containing 9% ash and 46 ppm fluoride and the second unit burned a bituminous coal from Gillette, Wyoming containing 5% ash and 45 ppm fluoride. It was thought that the greater mineral matter in the coal feeding the first unit may have played a role in the greater release of fluoride in the vapor phase from this unit. The concentration of hydrogen fluoride reported in emissions from a modern municipal waste incinerator in Germany was 0.2–0.3 mg/m^3 (Greim 1990). Fluoride concentrations in waste water from a coal-fired power plant in Utah ranged from 2.4 to 3.8 ppm (Miller et al. 1999).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The major sources of fluoride intake by the general population are water, beverages, food, and fluoride-containing dental products. Since levels in ambient air are, in most cases, below detectable limits, the levels inhaled are generally very low except for in areas immediately surrounding industries that emit fluorides into the air. Hodge and Smith (1977) estimated air intake of fluoride of about 0.01 mg/day. In occupational settings where airborne concentrations are frequently at the exposure limit of 2.5 mg/m^3 (OSHA 1985), fluoride intake via inhalation can be 16.8 mg/day, assuming an 8-hour shift and that a person inhales 20 m^3 air/day. The daily intake of fluoride from drinking water fluoridated at the optimal levels (0.7–1.2 mg/L) would be 1.4–2.4 mg.

The chemicals most commonly used by American waterworks are fluorosilicic acid, sodium silicofluoride, and sodium fluoride. Data from the CDC's 1992 Fluoridation Census indicate that 25% of utilities reported using sodium fluoride; however, this corresponds to 9.2% of the U.S. population drinking fluoride-supplemented tap water (Urbansky 2002). Concerns over the purity of water fluoridation agents have been raised as well as possible links between fluoridation agents and lead levels in the bloodstream (Masters et al. 2000). Analyses of available grades of fluorosilicic acid, sodium fluoride, and sodium fluorosilicate show the presence of arsenic and lead, but at levels far below that which would necessitate recommended maximum impurity content (RMIC) values based on the maximum dosage of 1.2 mg of fluoride ion per liter (NRC 1982).

Based on a comprehensive total diet study conducted in Winnipeg, Canada in 1987, the estimated daily dietary intake of fluoride by the average Canadian was 1,763 μg and varied from 353 μg for the 1–4-year-old-age group to 3,032 μg for 40–64-year-old males (Dabeka and McKenzie 1995). The results for all age groups are shown in Table 6-3. The drinking water used to prepare the food came from a single source containing the optimal fluoride concentration of 1 μg/mL (1 mg/L). This fluoride would contribute substantially to the fluoride intake in the food. In an earlier study in which the dietary intake of 24 adult Canadians was assessed, Dabeka et al. (1987) compared the intake of half of the participants who lived in communities with 1 μg/g (1 mg/L) fluoride in their drinking water with those who lived in communities with <0.2 μg/g (<0.2 mg/L) of fluoride in water. The respective median intakes of fluoride were 2,090 or 30.3 μg/kg/day and 414 or 7.0 μg/kg/day. For the cities with fluoridated water, the majority of fluoride was contributed by beverages (68%) and water (13%); for the nonfluoridated cites, beverages contributed 58% of the fluoride intake. These results can be compared with earlier estimates of fluoride intake by U.S. adults. San Filippo and Battistone (1971) estimated the average daily adult fluoride intake from food ranged from 0.8 to 0.9 mg, while the daily intake from food and water was 2.1–2.4 mg. Spencer et al. (1970) estimated the fluoride intakes as 1.2–2.7 mg/day from food and 2.82–5.9 mg/day from food and water. Kumpulainen and Koivistoinen (1977) reported the average total dietary intake in 12 fluoridated U.S. cities as 2.7 mg/day. In areas where fluoride is not added to water,

Table 6-3. Mean Daily Dietary Intake of Fluoride for Selected Canadian Population Groups[a]

Population	Mean daily intake (μg/day)
1–4 years, males and females	353
5–11 years, males and females	530
12–19 years, males and females	1,025
12–19 years, females	905
20–39 years, males	2,544
20–39 years, females	2,172
40–65 years, males	3,032
40–65 years, females	2,615
65+ years, males	2,588
65+ years, females	2,405
All ages male and female	1,763

[a] Dabeka and McKenzie 1995

the total intake from food and water does not usually exceed 1.0 mg/day (WHO 1984). However, there are exceptions, such as an area in China where the fluoride content of the water is low, but the intake from food and tea is high enough that the rate of dental fluorosis exceeds 80% (Han et al. 1995). In England, where much more tea is consumed, a study found daily average intakes of fluoride from tea to be 1.26 mg/day in children and 2.55 mg/day in adults (Cook 1969). In areas near sources of fluoride emissions, oral intake may also be increased from dust contamination of food (WHO 1984). Fluoridated dentifrices and mouth rinses are additional sources of fluoride (Barnhart et al. 1974; Ericsson and Forsman 1969). Fluorides approved by the FDA for use in dentifrices are sodium fluoride (0.22%), sodium monofluorophosphate (0.76%), and stannous fluoride (0.41%) (Pader 1993). The concentration of fluoride in each of these formulations is 0.1% (equivalent to 1,000 mg/kg or 1,000 ppm). Fluoride tablets or drops are ingested in some areas where water fluoride levels are low, providing 0.25, 0.50, or 1.00 mg/day depending on the age of the child and the drinking water fluoride concentration. In his analysis of systemic fluoride intake, Burt (1992) found that there is no evidence from dietary surveys to show that fluoride intake in adults has increased since the 1970s.

In considering dietary intake, it is important to take bioavailability into account, and not simply the fluoride content of the consumed substance. As discussed in Sections 2.3.1.2 and 2.8, absorption is affected by factors such as whether the material was eaten with a meal, the chemical and physical form of the fluoride, and the current health status of the individual (Rao 1984). The bioavailability of fluoride as sodium fluoride is high. In contrast, absorption of calcium fluoride is rather inefficient, but is enhanced when administered with food. Thus, the actual absorbed dose could be smaller than the intake levels reported above. NRC (1993) reports that approximately 75–90% of ingested fluoride is absorbed from the alimentary tract.

The fluoride content of urine and plasma are useful as short-term indicators of fluoride exposure; hair, fingernails, and tooth enamel are indicators of longer-term response. The mean and median serum fluoride levels of 168 representative Danish adults were 470±270 and 400 nmol/L (0.00893±0.00513 and 0.00760 mg/L), respectively (Poulsen et al. 1994). Levels were significantly higher in urban inhabitants than rural inhabitants and increased significantly with age. Shida et al. (1986) measured fluoride concentrations in five different layers of enamel of incisors that had been extracted due to periodontal disease. Half of the teeth were treated with 0.9% acidified fluorophosphate for 4 minutes. In the fluoride-treated group, the outer layer of enamel contained 1,660–5,910 ppm fluoride compared with 147–698 ppm in the untreated group. A similar method was employed by Schamschula et al. (1982) on enamel of children. They found that the fluoride content of enamel did reflect environmental fluoride exposure of the group, but variations occurred among individuals.

The NIOSH National Occupational Exposure Survey (NOES) conducted in 1981–1983 estimated that about 182,589 workers were potentially exposed to hydrogen fluoride (NIOSH 1989). The NOES was based on field surveys of 4,490 facilities that included virtually all workplace environments, except mining and agriculture, where eight or more persons are employed. The principal exposure pathway would be inhalation.

Workers in the electronics industry in Japan who used hydrogen fluoride for glass etching (e.g., TV picture tubes) and as a silicon cleaner (e.g., semiconductors) are exposed daily to mean air hydrogen fluoride concentrations of up to 5 ppm (Kono et al. 1987). The mean urinary fluoride levels were linearly related to the hydrogen fluoride concentration in the air and there were also significant differences in pre- and postshift urinary fluoride level of the workers. The workers in this study were only exposed to gaseous hydrogen fluoride. The wide variation of fluoride levels in serum and urine in the workers and controls has been ascribed to dietary differences, particularly the consumption of tea and seafood (water fluoridation is not practiced in Japan). In a follow-up study Kono et al. (1993) found a linear correlation between urine fluoride levels and hair fluoride levels.

A study evaluated the use of urinary fluoride as an exposure index for a prospective study of asthma in an aluminum smelter. In the first part of the study, 32 subjects wore personal air sampling pumps. The 12-hour time weighted average results show that overall mean levels were 15.7, 4.07, and 0.74 mg/m^3 for particulate mass, total fluoride, and hydrogen fluoride, respectively. Urinary fluoride concentrations were considered reasonably low, 1.3 and 3.0 mg/g creatinine in pre- and post-shift collections. Carbon smelters had the highest exposure levels as compared to workers working as potmen and trappers (Seixas et al. 2000). An average total fluoride exposure of 0.91 mg/m^3, of which 34% was gaseous fluoride, was measured for 41 workers in an aluminum plant in Sweden. Mean fluoride plasma concentrations were determined to be 23 and 48 ng/mL pre- and post-shift, respectively. Use of a safety mask during the shift led to a reduction in exposure of inhaled fluoride. Workers wearing a safety-mask throughout the whole shift reduced inhalation of fluoride to 30–40% of those workers not wearing masks (Ehrnebo and Ekstrand 1986).

Certain populations, such as patients with kidney disease, may be especially sensitive to fluoride exposure. In 1993, 20 patients became ill due to acute fluoride intoxication after receiving hemodialysis treatment for end-stage renal failure. This outbreak was found to be caused by errors in the maintenance of the deionization system used to treat the water used for dialysis. In this case, the deionization units continued to be used after the ion exchange resins were exhausted, resulting in the release of the resin-bound fluoride into the treated water (Arnow et al. 1994).

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).

Children are exposed to fluorides primarily through their diets and dental products. Normal dietary sources of fluorides are augmented by fluoridation of water supplies. Based on data obtained from a 1987 total diet study in Winnipeg, Canada, the average 1–4 and 5–11 year olds consume 353 and 530 μg fluoride/day, respectively, compared with 1,763 μg/day for all age groups combined (Dabeka and McKenzie 1995). The mean daily dietary intakes of fluoride by 6-month-old infants and 2-year-old children in four regions of the United States were 0.21–0.54 and 0.32–0.61 mg/day, respectively (NRC 1993; Ophaug et al. 1985). The mean intake of 2-year-old children, but not 6-month-old infants, was directly related to the fluoride concentration in the drinking water. Dietary intake may increase in areas where there are industrial emissions containing fluorides. Increased incidences of mottled teeth were observed in children living within 3 km of a superphosphate fertilizer plant in Port Maitland, Ontario (Sauriol and Gauthier 1984). The most plausible reason for the increased fluoride intake is higher fluoride levels in vegetables and fruits from dust deposited on the plants.

It has been assumed that children in communities without fluoridated water consume a negligible amount of fluoride other than from food. Because of the marked increase in dental fluorosis in nonfluoridated populations and the increased consumption of beverages that may have been prepared with fluoridated water, a study was conducted to estimate the average daily amount of fluoride ingested by a sample of North Carolinian children aged 2–10 from these beverages (Pang et al. 1992). The study found that children of ages 2–3, 4–6, and 7–10 consumed daily means of 0.36, 0.54, and 0.6 mg fluoride, respectively, from beverages. This is a significant source of fluoride intake. Beverages contributed about 60% of the children's total liquid consumption. While fluoride consumption increased with age, little difference was found between males and females. Children in a high fluoride area of Kenya consume high levels of fluoride from the water (9 ppm) and from the practice of giving tea to young children. In this area, children aged 0–1 and 1–4 years old had mean daily fluoride intakes of 0.62 and 1.23 mg/kg body weight, respectively. Tea accounted for nearly half of the fluoride intake of 1–2-year-old children. The daily fluoride consumption from breast milk supplements and substitutes averaged 7.6 mg, >250 times the amount of fluoride provided by 800 mL of breast milk (Opinya et al. 1991a).

Fluoride intake in infants depends on whether the child is nursed or not. Human breast milk contains very little fluoride (about 0.5 μmol/L or 0.01 mg/L) and provides <0.01 mg fluoride/day (NRC 1993). Fluoride intake by an infant who is exclusively breast fed and consuming 170 mL/kg-day is generally <2 μg/kg-day (Fomon and Ekstrand 1999). Levy et al. (2001) found that for most children, water fluoride intake was the predominant source of fluoride, especially through age 12 months. This was due in large part to children receiving fluoridated water mixed with infant formula concentrate (Levy et al. 1995b, 2001).

The results of a survey of fluoride levels in 68 samples of cows' milk and 115 samples of infant formulas and oral electrolytes are shown in Table 6-4. Mean fluoride levels in cows' milk, evaporated milk, and ready-to-use formula were 0.041, 0.23, and 0.79 μg/g, respectively. Mean levels in concentrated liquid and powder formula were 0.60 and 1.13 μg/g, respectively (Dabeka and McKenzie 1987). A major source of fluoride in the infant formulas appears to be the processing water used in its manufacture. In the United States where manufacturers remove fluoride from the processing water, mean levels of fluoride were much lower than in the Canadian products. All U.S. products were well within the upper guideline of 0.40 μg/g for ready-to-use formula proposed by the Committee on Nutrition of the American Academy of Pediatrics. Fluoride exposure was calculated to be 102, 105, and 167 μg/kg-day for infants consuming 170 mL/kg-day of concentrated liquid milk-based formula, concentrated liquid isolated soy protein-based formula, and powdered milk-based formula, respectively, which were diluted with water that is 1 ppm in fluoride. Infants may be exposed to higher fluoride concentrations now than in the past.

Table 6-4. Comparison of Fluoride Levels (μg/g) in Cow Milk and Infant Formulas[a]

	Number	Mean	Median	Range[a]
Cow milk	64	0.041	0.040	0.007–0.086
Evaporated milk	9	0.23	0.12	0.06–0.55
Ready-to-use formula, all				
Canadian	34	0.90	0.86	0.35–2.31
U.S.	7	0.23	0.26	0.15–0.28
Ready-to-use formula, glass[b]				
Canadian	20	0.82	0.83	0.46–1.13
U.S.	3	0.28	0.28	0.28–0.28
Ready-to-use formula, canned				
Canadian	14	1.02	0.95	0.35–2.31
U.S.	4	0.19	0.17	0.15–0.26
Concentrated liquid formula, canned	33	0.60	0.60	0.15–1.47
Formula, powdered concentrate	18	1.13	0.80	0.14–5.53
Electrolytes (water), glass[b]	12	0.066	0.04	0.01–0.15

[a] Dabeka and McKenzie 1995
[b] Product not available on retail market, obtained from hospitals.

In the 1960s, nearly 80% of infants were fed cow's milk by 6 months of age. In 1991, 80% of 6-month-old infants were fed formula (Fomon and Ekstrand 1999). Fluorinated organic chemicals are widely used and may accumulate in breast milk due to their high fat solubility and slow rate of metabolism and excretion. The breast milk fluoride concentration from a German study was 25 ppb (Broomhall and Kovar 1986). Fluoride may be an important mineral for babies born prematurely, since prematurity is associated with an increased incidence of dental caries; however, recommendations for fluoride intake are only available for full-term infants (Zlotkin et al. 1995).

Fluoridated dentifrices and mouth rinses are additional sources of fluoride, particularly in small children who do not have complete control of the swallowing reflex. Dentifrice ingestion was inversely correlated with age; average ingested levels per brushing for children aged 2–4, 5–7, and 11–13 were 0.30, 0.13, and 0.07 g (Barnhart et al. 1974). Average fluoride intake from these sources in children younger than 7 years old ranged from 0.3 to 0.4 mg/use for mouth rinses, depending on the child's age, and was about 0.1 mg/brushing for fluoridated toothpaste use (Ericsson and Forsman 1969). Other studies indicated that an average of 25% (range, 10–100%) of the toothpaste introduced into the mouth was swallowed. The average amount of fluoride in toothpaste used in one brushing is about 1.0 mg. From these studies, it has been estimated that the amount of fluoride ingested in toothpaste by children who live in communities with fluoridated water, who have good control of swallowing, and brush their teeth twice a day is approximately equal to dietary fluoride intakes. For younger children who have poor control of swallowing, intakes from dental products could exceed dietary intakes.

Although Burt (1992) concludes that data on fluoride intake by children from food and beverages, infant foods included, are not strong enough to conclude that an increase in fluoride ingestion has occurred since the 1970s, he warns that the suggested upper limit of fluoride intake is substantially being reached by many children by ingestion of fluoride from food and drink (0.2–0.3 mg/day) and from fluoride toothpaste (0.2–0.3 mg/day). Levy (1994) also found substantial variation in ingestion among individuals; 10–20% of individuals received up to several times as much exposure as the mean. Some children appeared to ingest enough fluoride from one source to exceed the total recommended fluoride intake, and are therefore at increased risk of dental fluorosis. Levy et al. (1995a) made the following recommendations concerning use of fluoride by children:

"(1) the fluoride content of foods and beverages, particularly infant formulas and water used in their reconstitution, should continue to be monitored closely in an effort to limit excessive fluoride intake;
(2) ingestion of fluoride from dentifrice by young children should be controlled, and the use of only small

quantities of dentifrice by young children should be emphasized; and (3) dietary fluoride supplements should be considered a targeted preventive regimen only for those children at higher risk for dental caries and with low levels of ingested fluoride from other sources (Levy et al. 1995a)."

Schamschula et al. (1985) analyzed various body fluids and tissue from a group of Hungarian children exposed to low, intermediate, and high levels of fluoride in their drinking water. These tissue levels, included in Table 6-5, are indicators of exposure over the short and long term. Fluoride dentifrices were not in general use in the villages from which the sample populations were drawn. Mean fluoride concentrations of 1.85, 5.28, and 7.52 mg/kg were found in fingernails of Brazilian children, 6–7 years old, living in communities where fluoride concentrations were 0.1, 1.6, and 2.3 ppm, respectively. Analysis of these data indicated a direct relationship between fluoride concentrations in drinking water and fingernails. The 95% confidence intervals for the 0.1 and 1.6–2.3 ppm areas showed no overlap; a small overlap was noted for the 1.6 and 2.3 ppm areas (Whitford et al. 1999a).

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Populations living in areas with high fluoride levels in groundwater may be exposed to higher levels of fluorides in their drinking water or in beverages prepared with the water. Among these populations, outdoor laborers, people living in hot climates, and people with polydipsia will generally have the greatest daily intake of fluorides because they consume greater amounts of water. Groundwater fluoride levels are especially high in the southwest; maximum groundwater levels in Nevada, southern California, Utah, New Mexico, and western Texas exceed 1,500 μg/L. In one region of northwest Texas, the median level in well water exceeded 4,000 μg/L. People who drink large amounts of tea or consume large quantities of seafood may also have high intakes of fluoride.

Populations living downwind of facilities emitting high levels of fluorides (e.g., phosphate fertilizer plants, aluminum plants, or coal-fired power plants) may be exposed to higher fluoride levels in the air (Ernst et al. 1986). Emissions from these plants may contaminate vegetables and fruit with fluorides from industrial emissions, exposing people eating local produce to potentially high levels of fluorides in their diets. Workers in industries where fluoride-containing substances are used, most notably the aluminum and phosphate fertilizer plants, may be occupationally exposed to high levels of both gaseous and particulate fluorides. Workers using sulfur hexafluoride as a tracer gas for determining ventilation rates

Table 6-5. Levels of Fluoride in Human Tissue and Urine—Selected Studies

Site	Population	Sample	Concentration	Type	Units	Reference
Human plasma from blood banks in five U.S. cites with different fluoride levels in drinking water						Guy et al. 1976
	Albany, NY (n=30) <0.1 ppm fluoride	Blood plasma	0.38 (0.14-1.1)	Mean (Range)	μmol/L	
	Rochester, NY (n=30) 1 ppm fluoride		0.89 (0.35-4.2)			
	Corpus Christi, TX (n=12) 0.9 ppm fluoride		1.0 (0.60-1.7)			
	Hillsboro, TX (n=4) 2.1 ppm fluoride		1.9 (0.60-2.6)			
	Andrews, TX (n=30) 5.6 ppm fluoride		4.3 (1.4-8.7)			
Poland (1980)						Miszke et al. 1984
	Employee of electrolysis shop of aluminum plant	Urine, random	1.87		mg/dm^3	
HF workers in the electronics industry, Japan						Kono et al. 1987
	Unexposed controls (n=82)	Urine, random	0.58 (0.23)	Geometric mean (GSD)	ppm	
	All workers (n=142)		2.34 (1.40)			
	Hydrogen fluoride exposure level					
	0.3 ppm (n=16)		0.91 (0.26)			
	0.5 ppm (n=20)		1.04 (0.34)			
	0.6 ppm (n=12)		1.07 (0.41)			
	1.2 ppm (n=14)		2.02 (0.57)			
	1.6 ppm (n=17)		2.40 (0.68)			
	2.8 ppm (n=21)		3.94 (1.07)			
	4.2 ppm (n=32)		5.05 (1.30)			
	5.0 ppm (n=10)		6.50 (1.98)			
HF workers in the electronics industry, Japan						Kono et al. 1993
	All hydrogen fluoride workers (n=142)	Hair	61.1 (101.6)	Geometric mean (GSD)	μg/g	
	Controls (n=237)		13.4 (6.4)			
HF workers, Japan						Kono et al. 1984
	Hydrogen fluoride workers (n=120)	Serum	40.10 (23.72)	Mean (SD)	μg/L	
	Controls (n=320)		24.50 (12.10)			
	Hydrogen fluoride workers (n=120)	Urine, 24 hour	0.98 (0.75)	Mean (SD)	mg/L	
	Controls (n=320)		0.54 (0.30)			

Table 6-5. Levels of Fluoride in Human Tissue and Urine—Selected Studies

Site Population	Sample	Concentration	Type	Units	Reference
Danish adults					Poulsen et al. 1994
Representative population (n=168)	Serum	470 (270)	Mean (SD)	nmol/L	
Brazilian children (6-7 years old) exposed to different water fluoride concentrations					Whitford et al. 1999a
Fluoride concentration in drinking water:					
0.1 ppm (n=19)	fingernail	1.85 (0.75-3.53)	Mean (range)	mg/kg	
1.6 ppm (n=12)		5.28 (2.28-7.53)			
2.3 ppm (n=15)		7.52 (4.00-13.18)			
Hungarian children exposed to three levels of fluoride in drinking water					Schamschula et al. 1985
Low exposure[a] (n=45)	Urine	0.15 (0.07)	Mean (SD)	ppm	
Medium exposure[b] (n=53)		0.62 (0.26)			
High exposure[c] (n=41)		1.24 (0.52)			
Low exposure[a] (n=45)	Nails	0.79 (0.26)	Mean (SD)	ppm	
Medium exposure[b] (n=53)		1.31 (0.49)			
High exposure[c] (n=41)		2.31 (1.14)			
Low exposure[a] (n=45)	Hair	0.18 (0.07)	Mean (SD)	ppm	
Medium exposure[b] (n=53)		0.23 (0.11)			
High exposure[c] (n=41)		0.40 (0.25)			
Low exposure[a] (n=45)	Saliva	6.25 (2.44)	Mean (SD)	ppb	
Medium exposure[b] (n=53)		11.23 (4.29)			
High exposure[c] (n=41)		15.87 (6.01)			
Low exposure[a] (n=45)	Enamel (0.44–0.48 μm depth)	1,549 (728)	Mean (SD)	ppm	
Medium exposure[b] (n=53)		2,511 (1,044)			
High exposure[c] (n=41)		3,792 (1,362)			
Low exposure[a] (n=45)	Enamel (2.44–2.55 μm depth)	641 (336)	Mean (SD)	ppm	
Medium exposure[b] (n=53)		1,435 (502)			
High exposure[c] (n=41)		2,107 (741)			

[a] Low exposure: concentration of fluoride in water 0.06–0.11 ppm, 0.09 ppm, mean.
[b] Medium exposure: concentration of fluoride in water 0.5–1.1 ppm, 0.82 ppm, mean.
[c] High exposure: concentration of fluoride in water 1.6–3.1 ppm, 1.91 ppm, mean.

GSD = geometric standard deviation; SD = standard deviation and air flow in buildings may be exposed to hydrogen fluoride when unvented combustion sources are present in the building because SF_6 reacts with water vapor at high temperatures, forming hydrogen fluoride (Guo et al. 2001).

Populations living in the vicinity of hazardous waste sites may be exposed to fluorides through contact with contaminated air, water, and soil. Food grown near the source may also be contaminated. Data on the concentrations of fluorides in waste site media are quite limited, and no information was located regarding daily intake of fluorides from these sources.

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

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. The physical/chemical properties of fluorine, hydrogen fluoride, and sodium fluoride are sufficiently well characterized to enable assessment of the environmental fate of these compounds.

Production, Import/Export, Use, Release, and Disposal. Information on the production and importation of fluorspar and hydrogen fluoride are available (CMR 2002; USGS 2001). Information on exports is only available for fluorspar. No data are available on the production, import, or export of fluorine, sodium fluoride, and other fluorides. Information is readily available on the uses of fluorine, hydrogen fluoride, and other fluorides (Mueller 1994). Because of its high reactivity, fluorine is disposed of by conversion to fluoride salts in a scrubber (Shia 1994). The TRI contains information on the amounts of hydrogen fluoride transferred off-site, presumably for disposal, and the amount recycled. No information was found regarding the disposal of sodium fluoride. Additional quantitative information on production, import, and export of fluorides, as well as common disposal practices, would be useful in assessing the release of, and potential exposure to, these compounds.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to EPA. The TRI, which contains this information for 2001, is currently available. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. Upon release to the atmosphere, fluorine gas will readily react to form hydrogen fluoride. Both hydrogen fluoride and particulate fluorides will be transported in the atmosphere and deposited on land or water by wet and dry deposition. Fluorides undergo transformations in soil and water, forming complexes and binding strongly to soil and sediment (NAS 1971a; WHO 1984). Information on the environmental fate of fluorides is sufficient to permit a general understanding of the widespread transport and transformation of fluorides in the environment.

A recent review (Urbansky 2002) looked at the fate of fluorosilicate drinking water additives. Various fluorosilicates and aquo/hydroxo/oxo/fluorosilicates may exist in fluoridated water systems and these species may occur, regardless of the fluoridating agent used, since water may contain natural silica. The author states that it would be desirable to be able to identify and measure or calculate concentrations of those species that do exist and rule out those that do not exist (Urbansky 2002).

Bioavailability from Environmental Media. Fluorides are absorbed by humans following inhalation of workplace and ambient air that has been contaminated (Chan-Yeung et al. 1983a; Waldbott 1979), ingestion of drinking water and foods (Carlson et al. 1960a; Spencer et al. 1970), and dermal contact (Browne 1974; Buckingham 1988). Information is available on factors that influence bioavailability of ingested fluoride (Rao 1984). However, this information is rarely coupled with the available information on total ingested fluoride to determine actual bioavailable dose. Additional information on absorption following ingestion of contaminated soils (i.e., by children) would be useful in determining the bioavailability of fluorides from these routes of exposure, which may be of particular importance for populations living in the vicinity of hazardous waste sites.

Food Chain Bioaccumulation. Fluorides have been shown to accumulate in animals that consume fluoride-containing foliage (Hemens and Warwick 1972). However, accumulation is primarily in skeletal tissue and therefore, it is unlikely that fluoride will biomagnify up the food chain.

Exposure Levels in Environmental Media. Fluorides have been detected in ambient air, surface water, groundwater, drinking water, and foods (Barnhart et al. 1974; Davis 1972; EPA 1980a; Hudak 1999; Waldbott 1963b). However, the existing monitoring data are not current. Air concentrations are expected to be different today in view of changes in industries and the wider use of pollution control devises. Recent serial measurements of fluorides in air are needed. Groundwater contains higher fluoride levels than surface water. Although Fleischer (1962) mapped the levels of fluoride in groundwater in the United States and these levels would not be expected to change, it would be useful to survey the concentration of fluoride in groundwater used for drinking. This is particularly important in areas where groundwater has high fluoride content, as in northwest Texas where 50% of the well water in some counties exceed 4 μg/L (Hudak 1999). The fluoride level in food depends on the locality in which the food is grown, including the geology, potential sources of fluorine emissions in the area, the amount of fertilizer and pesticides applied, the type of processing the food receives, and whether fluoridated water is used in food preparation (McClure 1949; Myers 1978; Waldbott 1963b). Foods characteristically high in fluoride content include tea, seafood, and bone products such as bone meal and gelatin (Cook 1969; Kumpulainen and Koivistoinen 1977). Old estimates of intake via ingestion have been made for members of the general population (Kumpulainen and Koivistoinen 1977; NAS 1971a; Spencer et al. 1970; WHO 1984). Recent data are available on the concentration of fluoride in different foods in Canada and the daily dietary intakes for different Canadian age groups (Dabeka and McKenzie 1995). However, recent analogous information is not available for the United States. Up-to-date data on concentrations of fluoride in food items and the dietary intake of fluorides in the United States is important in view of the changes in fluoride emissions and the effect that the use of fluoridated water or water with a high natural fluoride content may have on the fluoride levels in processed food and beverages (Pang et al. 1992).

Fluorides have also been detected in a limited number of surface water, groundwater, and soil samples taken at hazardous waste sites (HazDat 2003; Van Hook 1974). Additional information is needed on concentrations in ambient air, surface water, groundwater, and soils at these waste sites. This information will be helpful in estimating exposures of populations living near these sites through contact with contaminated media.

Exposure Levels in Humans. Fluorides can be measured in urine, plasma, saliva, tooth enamel, nails, bone, and other tissues. Detection of fluoride in biological tissues, particularly urine, has been used as an indicator of human exposure to fluorides in the workplace and through consumption of fluoridated drinking water (Chan-Yeung et al. 1983a; Kaltreider et al. 1972; Spencer et al. 1970). Additional data on fluoride levels in urine and other fluids and tissues are needed for populations living near hazardous waste sites. This information will be helpful in establishing exposure profiles for waste site populations that may be exposed to higher than background levels of fluorides through contact with contaminated media. The total human intake is of interest, since multiple sources, all of which are generally considered safe by themselves, could, under some circumstances, provide total intake that is considered to be above the "safe" level.

Exposures of Children. Children are exposed to fluorides primarily through their diets and the use of dental products, particularly toothpaste. Normal dietary sources of fluorides are augmented by fluoridation of water supplies. Human breast milk contains very little fluoride (NRC 1993). Information is available on the levels of fluoride in infant formula in Canada and results show that major source of fluoride appears to be the processing water used in its manufacture (Dabeka and McKenzie 1987). In the United States, manufacturers remove fluoride from the processing water and thus, fluoride levels in infant formulas are much lower. The mean dietary intake of fluoride by infants and children is available for Winnipeg, Canada and four regions of the United States (Dabeka and McKenzie 1995; Fomon and Ekstrand 1999; NRC 1993). The mean daily dietary intakes of fluoride by 6-month-old infants and 2-year-old children in four regions of the United States were 0.21–0.54 and 0.32–0.61 mg/day, respectively. The mean intakes of 2 year olds, but not 6 month olds, were directly related to the fluoride concentration in the drinking water. Pang et al. (1992) noted that children obtain a sizeable amount of fluoride from beverages. Infants may be exposed to higher fluoride concentrations now than in the past. While nearly 80% of infants were fed cow's milk by 6 months of age in the 1960s, in 1991, 80% of 6-month-old infants were fed formula, which contains higher fluoride concentrations than either human or cow's milk (Fomon and Ekstrand 1999). Since beverages may not be prepared with water from the local community and beverages constitute 60% of children’s total liquid consumption, more information on the fluoride content of beverages would be useful in estimating children’s dietary intake of fluoride. Intake of fluoride by children from fluoridated dentifrices and mouth rinses have been estimated (Barnhart et al. 1974; Ericsson and Forsman 1969). For younger children who have poor control of swallowing, intakes from dental products could exceed dietary intakes. Fluoride may be an important mineral for babies born prematurely, since prematurity is associated with an increased incidence of dental caries; however, recommendations for fluoride intake are only available for full-term infants (Zlotkin et al 1995).

Fluoride exposure in communities near mining and other industrial facilities where fluoride-containing rock or minerals are processed are a public health concern, especially for infants and children. The same is true for hazardous waste sites containing fluoride waste. Since fluoride remains in the surface soil indefinitely and long past land uses may be forgotten, people may not realize that they are living in areas where high levels of fluoride may occur in soil. Contaminated soils pose a particular hazard to children because of both hand-to-mouth behavior and intentional ingestion of soil (pica) that contains fluorides and other contaminants. In these communities, fluorides may have been tracked in from outdoors and contaminate carpeting. Fluoride-containing dust may be brought home in the clothing of parents working in industries where they are exposed to fluoride. Children may be exposed to this fluoride while crawling around or playing on contaminated carpeting. Exposure may also result from dermal contact with soil, or by inhaling dust and then swallowing it after mucociliary transport up out of the lungs. Because much of the fluoride in soil is embedded in or strongly adsorbed to soil particles or insoluble, it may not be in a form accessible for uptake by the body.

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 fluorides were located. This compound is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The compound will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to this compound.

6.8.2 Ongoing Studies

The Federal Research in Progress (FEDRIP 2002) 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.

Remedial investigations and feasibility studies conducted at the 188 NPL sites known to be contaminated with fluorine, hydrogen fluoride, or fluorides may add to the existing database on exposure levels in environmental media at hazardous waste sites, exposure levels in humans, and exposure registries.

J.G. Schumacher of USGS, Water Resources Division, Weldon Spring, Missouri, is doing research sponsored by USGS to determine the geochemical controls on contaminant migration from the raffinate pits, Weldon Spring chemical plant, St. Charles County, Missouri. The former U.S. army facility processed uranium ore-concentrates and scrap into uranium trioxide, uranium tetrafluoride, and uranium metal. Waste from these operations (referred to as raffinate) was pumped into four large pits that contain various quantities of uranium, thorium, nitrate, sulfate, fluoride, magnesium, and other elements. The raffinate pits have been determined to be leaking and Li, U, NO_3, and SO_4, and various trace elements have been found in groundwater and surface water both on and off site.

No other ongoing studies pertaining to the environmental fate of fluorine, hydrogen fluoride, or fluorides were identified.