

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Barium is a naturally occurring component of minerals that are found in small but widely distributed amounts in the earth's crust, especially in igneous rocks, sandstone, shale, and coal (Kunesh 1978; Miner 1969a). Barium enters the environment naturally through the weathering of rocks and minerals. Anthropogenic releases are primarily associated with industrial processes. Barium is present in the atmosphere, urban and rural surface water, soils, and many foods.

Under natural conditions, barium is stable in the +2 valence state and is found primarily in the form of inorganic complexes. Conditions such as pH, Eh (oxidation-reduction potential), cation exchange capacity, and the presence of sulfate, carbonate, and metal oxides will affect the partitioning of barium and its compounds in the environment. The major features of the biogeochemical cycle of barium include wet and dry deposition to land and surface water, leaching from geological formations to groundwater, adsorption to soil and sediment particulates, and biomagnification in terrestrial and aquatic food chains.

The general population is exposed to barium through consumption of drinking water and foods, usually at low levels. Workers in barium mining or processing industries and individuals who reside near such industries might be exposed to relatively high levels, primarily through the inhalation of fugitive dust containing barium compounds. The most recent occupational exposure estimates indicate that about 10,000 people were potentially exposed to barium and about 474,000 to barium compounds in workplace environments in the United States in 1980.

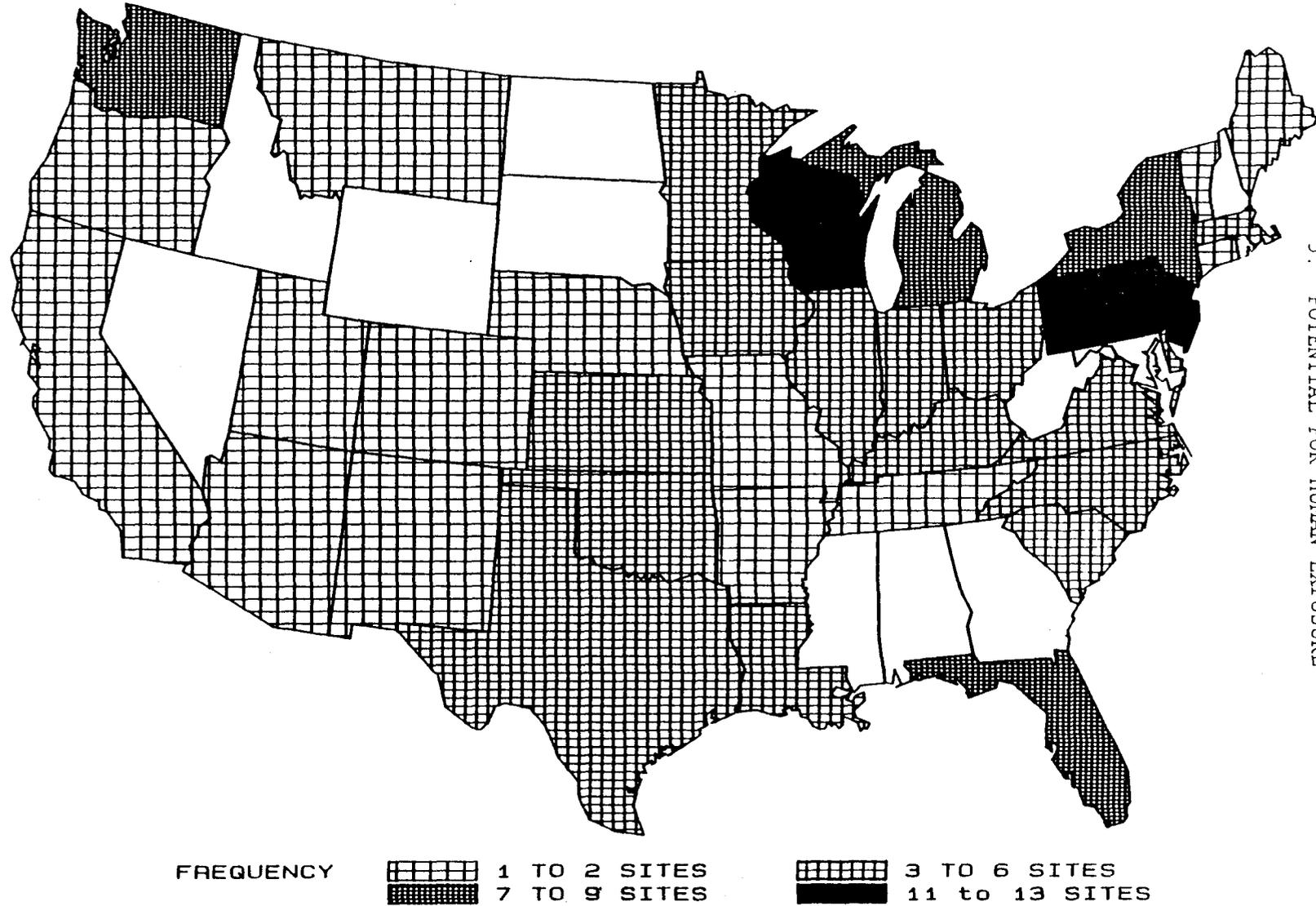
EPA has identified 1,177 NPL sites. Barium has been found at 154 of the total number of sites evaluated for barium. Barium cyanide and barium carbonate have also been found at 1 and 8 sites, respectively (View 1989). However, we do not know how many of the 1,177 sites have been evaluated for barium, barium cyanide, or barium carbonate. As more sites are evaluated by EPA, these numbers may change. The frequency of these sites within the United States can be seen in Figure 5-1.

5.2 RELEASES TO THE ENVIRONMENT

Barium is a highly reactive metal that occurs naturally only in a combined state. The element is released to environmental media by both natural processes and anthropogenic sources.

According to the SARA Section 313 Toxics Release Inventory (TRI), an estimated total of 16.3 million pounds of barium and barium compounds were released to the environment from manufacturing and processing facilities in

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



* Derived from View 1989

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the United States in 1987 (TRI 1989) (see Table 5-1). Most of these barium releases were to land, The quality of the TRI data must be viewed with caution since the 1987 data represent first-time, incomplete reporting of estimated releases by these facilities. Only certain types of facilities were required to report. This is not an exhaustive list.

5.2.1. Air

Barium is released primarily to the atmosphere as a result of industrial emissions during the mining, refining, and production of barium and barium chemicals, fossil fuel combustion (Miner 1969a), and entrainment of soil and rock dust into the air (Schroeder 1970). In addition, coal ash, containing widely variable amounts of barium, is also a source of airborne barium particulates (Miner 1969a; Schroeder 1970). In 1969, an estimated 18% of the total U.S. barium emissions to the atmosphere resulted from the processing of barite ore, and more than 28% of the total was estimated to be from the production of barium chemicals. The manufacture of various end products (e.g., drilling well muds, and glass, paint, and rubber products) and the combustion of coal were estimated to account for an additional 23% and 26% of the total barium emissions for 1969, respectively (Davis 1972).

According to TRI, an estimated total of 0.6 million pounds of barium and barium compounds were released to the atmosphere from manufacturing and processing facilities in the United States in 1987 (TRI 1989).

Estimates of barium releases from individual industrial processes are available for particulate emissions from the drying and calcining of barium compounds and for fugitive dust emissions during the processing of barite ore. Soluble barium compounds (unspecified) are emitted as particulates from barium chemical dryers and calciners to the atmosphere during the processing of barium carbonate, barium chloride, and barium hydroxide (Reznik and Toy 1978). Uncontrolled particulate emissions of soluble barium compounds from chemical dryers and calciners during barium processing operations may range from 0.04 to 10 g/kg of final product. Controlled particulate emissions are less than 0.25 g/kg of final product. Based on an uncontrolled emission factor of 5 g/kg and a controlled emission factor of 0.25 g/kg, total particulate emissions from the drying and calcining of barium carbonate, barium chloride, and barium hydroxide are estimated to be 160 metric tons (352,800 pounds) per year (Reznik and Toy 1978).

Fugitive dust emissions occur during processing (grinding and mixing) of barite ore and may also occur during the loading of bulk product of various barium compounds into railroad hopper cars (Reznik and Toy 1978). Based on an emission factor of 1 g/kg, total emissions of fugitive dust from the domestic barium chemicals industry during the grinding of barite ore have been estimated to be approximately 90 metric tons (198,450 pounds) per year (Reznik and Toy 1978). Other particulate emissions from the industrial production of barium compounds include an estimated 820 metric tons (1.8 million pounds) per

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

State ^c	No. of facilities	Range of reported amounts released in thousands of pounds ^b						
		Air	Underground injection	Water	Land	Total Environment ^d	POTW ^e transfer	Off-site waste
AL	9	0-2.3	0-0	0-0.3	0-9.3	0-9.6	0-0.1	0-16
AR	2	0.3-0.3	0-0	0-0	0-0	0.3-0.3	0-0	0-2.5
AZ	3	0-0.3	0-0	0-0	0-5,300	0-5,300	0-0	0-0
CA	34	0-7.9	0-2.4	0-5.5	0-16.2	0-24.5	0-0.3	0-73.7
CO	4	0-0.6	0-0	0-0.1	0-0	0-0.8	0-0	0-346
CT	10	0-0.5	0-0	0-0.3	0-0	0-0.8	0-0.3	0-78.5
DE	1	0.5-0.5	0-0	0-0	0-0	0.5-0.5	0.6-0.6	0-0
FL	3	0-0.3	0-0	0-0	0-0	0-0.3	0-0	0-59.2
GA	12	0-9.5	0-0	0-17	0-0.1	0-26.5	0-1.2	0-4,300
IA	11	0-0.3	0-0	0-0.1	0-5	0-5	0-0.1	0-4.3
ID	2	0-0.5	0-0	0-1	0-180.3	0-181.8	0-0.3	0-0.3
IL	29	0-1.8	0-0	0-0.3	0-1,161	0-1,163	0-0.8	0-1,639
IN	16	0-4.7	0-0.3	0-0.1	0-0.3	0-4.7	0-5.4	0-56.6
KS	3	0-0.3	0-0	0-0	0-0.5	0-0.5	0-0.3	0-0.5
KY	16	0-2.2	0-0	0-0.5	0-207.3	0-207.3	0-6.8	0-91.2
LA	10	0-36.6	0-0	0-0.3	0-0	0-36.6	0-0.3	0-34.3
MA	7	0-2.3	0-0	0-0	0-0	0-2.3	0-0.3	0-37
MD	8	0-6.1	0-0	0-2.2	0-0	0-6.1	0-0.3	0.3-60
MI	38	0-16	0-0	0-2	0-1.9	0-16	0-46	0-1,800
MN	4	0.3-18	0-0	0-1	0-4.2	0.3-18	0.3-0.3	0-1.4
MO	16	0-14.7	0-0	0-0.3	0-0.1	0-14.7	0-120	0-66
MS	4	0-1.1	0-0	0-0	0-0.3	0-1.1	0-0	0-1.2
NC	15	0-6.1	0-0	0-0	0-100.3	0-100.3	0-2.1	0-252.3
ND	2	0.3-0.3	No Data	0-0	0-0.3	0.5-0.5	0-0	0-0
NE	4	0-0.3	0-0	0-0	0-0	0-0.3	0-0	0-84.2
NJ	32	0-6.2	0-0	0-0.3	0-144.5	0-144.7	0-42.1	0-93.5
NM	1	0-0	0-0	0-0	0-0	0-0	0-0	0-0
NV	1	8.5-8.5	0-0	0-0	0-0	8.5-8.5	0-0	0-0
NY	28	0-14.8	0-0	0-16	0-88	0-93.7	0-130	0-385.2
OH	76	0-58.8	0-0	0-180	0-10.5	0-180	0-24.6	0-45.4
OK	10	0-0.4	0-0	0-0.3	0-0.3	0.1-0.5	0-0.1	0-1.4
OR	2	0.5-0.5	0-0	0-0.8	0-0	0.5-1.3	0-0	1.2-108
PA	39	0-1.1	0-0	0-1.6	0-154.7	0-155.2	0-10.9	0-93.7
PR	1	0-0	0-0	0-0	0-0	0-0	44-44	0-0

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TABLE 5-1 (Continued)

State ^c	No. of facilities	Range of reported amounts released in thousands of pounds ^b						
		Air	Underground injection	Water	Land	Total Environment ^d	POTW ^e transfer	Off-site waste
RI	2	0-1.9	0-0	0-0	0-0	0-1.9	0-0	0-0
SC	6	0-9.8	0-0	0-0	0-67.9	0-67.9	0-12.5	0-67.9
TN	10	0-2.8	0-0	0-0.3	0-18	0-18	0-93.9	0-619.4
TX	34	0-262	0-0	0-4	0-109	0-262	0-0.5	0-100
UT	6	0-9.2	0-0	0-0.3	0-6,900	0-6,909	0-0	0-8.4
VA	9	0-21.5	0-0	0-0.3	0-0.5	0-21.5	0-0.3	0-32
VT	2	0.1-0.3	0-0	0-0	0-0	0.1-0.3	0-0	3.6-37.8
WA	3	0-86	0-0	0-0	0-1.6	0-87.6	0-0	0-1.3
WI	10	0-4.3	0-0.3	0-1.1	0-0	0.1-4.3	0-4.6	0-78.9
WV	4	0-0.8	0-0	0-0.9	0-0	0-0.9	0-0.3	0-18

^aTRI 1989

^bData in TRI are maximum amounts released by each facility. Quantities reported here have been rounded to the nearest hundred pounds, except those quantities > 1 million pounds which have been rounded to the nearest thousand pounds.

^cPost office state abbreviation

^dThe sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility.

^ePublicly owned treatment works

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year from uncontrolled kilns during the processing of barite ore and 8 metric tons (17,640 pounds) per year from black ash (i.e., barium sulfide) rotary kilns during the production of barium hydroxide (Reznik and Toy 1978).

The use of barium in the form of organometallic compounds as a smoke suppressant in diesel fuels results in the release of solids to the atmosphere (Miner 1969a; Ng and Patterson 1982; Schroeder 1970). The maximum concentration of soluble barium in exhaust gases containing barium-based smoke suppressants released from test diesel engines and operating diesel vehicles is estimated to be 12,000 mg/m³, when the barium concentration in the diesel fuel is 0.075% by weight and 25% of the exhausted barium (at a sampling point 10 ft from the engine and upstream from the muffler) is soluble (Golothan 1967). Thus, 1 L of this exhaust gas contains an estimated 12 mg soluble barium or 48 mg total barium (Schroeder 1970).

5.2.2 Water

The primary source of naturally occurring barium in drinking water results from the leaching and eroding of sedimentary rocks into groundwater (Kojola et al. 1978). Although barium occurs naturally in most surface water bodies (i.e., approximately 99% of those examined) (Kopp and Kroner 1967), releases of barium to surface waters from natural sources are much lower than those to groundwater (Kojola et al. 1978).

About 80% of the barium produced is used as barite to make high-density oil and gas well drilling muds, and during offshore drilling operations there are periodic discharges of drilling wastes in the form of cuttings and muds into the ocean (Ng and Patterson 1982). For example, in the Santa Barbara Channel region, about 10% of the muds used are lost into the ocean (Ng and Patterson 1982). The use of barium in offshore drilling operations may increase barium pollution, especially in coastal sediments (Ng and Patterson 1982).

Barium has been detected with a positive geometric mean concentration of 101.6 mg/L in groundwater samples from approximately 58% of the 2,783 hazardous waste sites that have had samples analyzed by the Contract Laboratory Program (CLP) (CLPSD 1989). Barium has also been detected with a positive geometric mean of 62.6 mg/L in surface water samples from 27% of the sites in the CLP statistical database (CLPSD 1989). Note that these data from the CLP Statistical Database (CLPSD) represent frequency of occurrence and concentration information for NPL sites only.

According to TRI, an estimated total of 312,000 pounds of barium and barium compounds were released to surface waters from manufacturing and processing facilities in the United States in 1987 (TRI 1989).

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5.2.3 Soil

The process of drilling for crude oil and natural gas generates waste drilling fluids or muds, which are often disposed of by land farming. Most of these fluids are water based and contain barite and other metal salts. Thus barium may be introduced into soils as the result of land farming these slurried reserve pit wastes (Bates 1988).

The use of barium fluorosilicate and carbonate as insecticides (Beliles 1979; Meister 1989) might also contribute to the presence of barium in agricultural soils.

According to TRI, an estimated total of 14.9 million pounds of barium and barium compounds were released to soils from manufacturing and processing facilities in the United States in 1987 (TRI 1989).

Barium has been detected with a positive geometric mean concentration of 100.5 ppm in soil samples from approximately 52% of the hazardous waste sites that have had samples analyzed by the CLP (CLPSD 1989). Note that these data from the CLPSD represent frequency of occurrence and concentration data for NPL sites only.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Most barium released to the environment from industrial sources is in forms that do not become widely dispersed (Ng and Patterson 1982). In the atmosphere, barium is likely to be present in particulate form (EPA 1984). Although chemical reactions may cause changes in speciation of barium in air, the main mechanisms for the removal of barium compounds from the atmosphere are likely to be wet and dry deposition (EPA 1984).

In aquatic media, barium is likely to precipitate out of solution as an insoluble salt (i.e., as $BaSO_4$ or $BaCO_3$). Waterborne barium may also adsorb to suspended particulate matter (Bodek et al. 1988; EPA 1984; Lagas et al. 1984). Precipitation of barium sulfate salts is accelerated when rivers enter the ocean because of the high sulfate content in the ocean (Bowen 1966). Sedimentation of suspended solids removes a large portion of the barium content from surface waters (Benes et al. 1983). Barium in sediments is found largely in the form of barium sulfate (barite). Coarse silt sediment in a turbulent environment will often grind and cleave the barium sulfate from the sediment particles leaving a buildup of dense barites (Merefield 1987). Estimated soil: water distribution coefficients (K_d) (i.e., the ratio of the quantity of barium sorbed per gram of sorbent to the concentration of barium remaining in solution at equilibrium) range from 200 to 2,800 for sediments and sandy loam soils (Baes et al. 1984; Rai et al. 1984).

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The uptake of barium by fish and marine organisms is also an important removal mechanism (Bowen 1966; Schroeder 1970). Barium levels in sea water range from 2 to 63 mg/L with a mean concentration of about 13 µg/L (Bowen 1979). Barium was found to bioconcentrate in marine plants by a factor of 1,000 times the level present in the water. Bioconcentration factors in marine animals, plankton, and in brown algae of 100, 120, and 260, respectively, have been reported (Bowen 1966; Schroeder 1970).

Barium added to soils (e.g., from the land farming of waste drilling muds) may either be taken up by vegetation or transported through soil with precipitation (Bates 1988). Relative to the amount of barium found in soils, little is bioconcentrated by plants (Schroeder 1970). However, this transport pathway has not been comprehensively studied.

Barium is not very mobile in most soil systems. The rate of transportation of barium in soil is dependent on the characteristics of the soil material. Soil properties that influence the transportation of barium to groundwater are cation exchange capacity and calcium carbonate (CaCO₃) content. In soil with a high cation exchange capacity (e.g., fine textured mineral soils or soils with high organic matter content), barium mobility will be limited by adsorption (Bates 1988; Kabata-Pendias and Pendias 1984). High CaCO₃ content limits mobility by precipitation of the element as BaCO₃ (Lagas et al. 1984). Barium will also precipitate as barium sulfate in the presence of sulfate ions (Bodek et al. 1988; Lagas et al. 1984). Barium is more mobile and is more likely to be leached from soils in the presence of chloride due to the increased solubility of barium chloride as compared to other chemical forms of barium (Bates 1988; Lagas et al. 1984). Barium complexes with fatty acids (e.g., in acidic landfill leachate) will be much more mobile in the soil due to the lower charge of these complexes and subsequent reduction in adsorption capacity (Lagas et al. 1984).

Barium mobility in soil is reduced by the precipitation of barium carbonate and sulfate. Humic and fulvic acid have not been found to increase the mobility of barium (EPA 1984).

5.3.2 Transformation and Degradation

5.3.2.1 Air

Elemental barium is oxidized readily in moist air (EPA 1983a, 1987a; Kunesh 1978). The residence time of barium in the atmosphere may be several days, depending on the size of the particulate formed, the chemical nature of the particulate, and environmental factors such as rainfall (EPA 1984).

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5.3.2.2 Water

Under natural conditions barium will form compounds in the +2 oxidation state. Barium does not hydrolyze appreciably except in highly alkaline environments (i.e., at pH levels greater than or equal to 10) (Bodek et al. 1988).

Appreciable levels of barium sulfate occur because natural water often contains high sulfate concentrations. Since the solubility of barium sulfate is low, only trace amounts of barium dissolve in surface water (Bodek et al. 1988; NAS 1977). At pH levels of 9.3 or below, barium sulfate may limit barium concentrations in natural waters (Bodek et al. 1988). The solubility of barium sulfate increases considerably in the presence of chloride (Cl^-) and other anions (e.g., NO_3^- and CO_3^{2-}), and at pH levels of 9.3 or below, the barium ion (Ba^{+2}) is the dominant species (Bodek et al. 1988; NAS 1977). The Ba^{+2} ion is stable under the pH-Eh range of natural systems. However, natural and treated waters usually contain sufficient sulfate so that a barium ion concentration of more than 1,000-1,500 mg/L cannot be maintained in solution (EPA 1983a; Hem 1959; Lagas et al. 1984; McCabe et al. 1970).

As pH levels increase above 9.3 and in the presence of carbonate, barium carbonate becomes the dominant species (Bodek et al. 1988; Singer 1974). Barium carbonate also exhibits fast precipitation kinetics and very low solubility and in alkaline environments limits the soluble barium concentration (Faust and Aly 1981; Hem 1959; Rai et al. 1984; Singer 1974). Barium forms salts of low solubility with arsenate, chromate, fluoride, oxalate, and phosphate ions (Bodek et al. 1988; EPA 1983a; Kunesh 1978). The chloride, hydroxide, and nitrate of barium are water-soluble (Bodek et al. 1988; EPA 1983a; Kirkpatrick 1978) and are frequently detected in aqueous environments (Rai et al. 1984).

Barium also forms complexes with natural organics in water (e.g., fatty acids in acidic landfill leachates) to a limited extent (Lagas et al. 1984; Morel 1983; Rai et al. 1984).

5.3.2.3 Soil

Barium reacts with metal oxides and hydroxides in soil and is subsequently adsorbed onto soil particulates (Hem 1959; Rai et al. 1984). Adsorption onto metal oxides in soils and sediments probably acts as a control over the concentration of barium in natural waters (Bodek et al. 1988). Under typical environmental conditions, barium displaces other adsorbed alkaline earth metals from MnO_2 , SiO_2 , and TiO_2 , (Rai et al. 1984). However, barium is displaced from Al_2O_3 by other alkaline earth metals (Rai et al. 1984). The ionic radius of the barium ion in its typical valence state (Ba^{+2}) makes isomorphous substitution possible only with strontium and generally not with the other members of the alkaline earth elements (Kirkpatrick 1978). Among

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the other elements that occur with barium in nature, substitution is common only with potassium but not with the smaller ions of sodium, iron, manganese, aluminum, and silicon (Kirkpatrick 1978).

Barium is also adsorbed onto soil and subsoil through electrostatic interactions (Bodek et al. 1988; Singer 1974). The cation exchange capacity of the sorbent largely controls the retention of barium in soils (Bodek et al. 1988). Barium is strongly adsorbed by clay minerals (Kabata-Pendias and Pendias 1984; Lagas et al. 1984).

Barium can also form salts with acetate, nitrate, chloride, and hydroxide ions in soil. The mobility of barium in soils increases upon formation of these water soluble salts (Bodek et al. 1988). In general, the solubility of barium compounds increases with decreasing pH.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Urban and suburban air concentrations have been found to range from less than 0.005 to 1.5 mg/m³ (Tabor and Warren 1958). No distinct pattern related to industrialization appeared in the results reported on 754 samples from 18 cities and four suburban areas in the United States. For example, in Houston, Texas and its suburbs, 76% of the samples contained barium at levels ranging from 0.005 to 1.5 mg/m³, whereas in Fort Worth, Texas, 66% of the samples had values below 0.005 mg/m³ (Tabor and Warren 1958).

A more recent compilation of atmospheric data shows barium concentrations in urban atmospheres of North America ranging from 2×10^{-4} to 2.8×10^{-2} µg/m³ with a mean concentration of 1.2×10^{-2} µg/m³ (Bowen 1979). In contrast, barium levels in samples from the South Pole and northern Norway were 1.6×10^{-5} and 7.3×10^{-4} µg/m³, respectively (Bowen 1979).

Maximum ground-level barium concentrations (as soluble compounds) associated with uncontrolled atmospheric particulate emissions from chemical dryers and calciners at barium-processing plants have been estimated (using dispersion modeling) to range from 1.3 to 330 mg/m³ over a 24-hour averaging time at locations along facility boundaries (i.e., away from the source of emission) (Reznik and Toy 1978).

5.4.2 Water

Barium has been found in almost all raw surface waters and public drinking water supplies sampled (i.e., approximately 99%) (Kopp 1969) at concentrations ranging from about 2 to 380 mg/L with mean concentrations generally on the order of 10 to 60 mg/L (Barnett et al. 1969; Bowen 1979; Durfor and Becker 1964; Durum and Haffty 1961; Kopp 1969; Kopp and Kroner 1967; McCabe et al. 1970; Tuovinen et al. 1980).

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Barium concentrations in groundwater supplies have been known to exceed EPA's maximum contaminant level (MCL) of 1.0 mg/L (1,000 mg/L); this may be due to leaching and erosion of barium from sedimentary rocks (Calabrese 1977; Kojola et al. 1978). For example, community water supplies from deep rock and drift wells in northeastern Illinois have been found to have barium concentrations ranging from 1,100 to 10,000 mg/L (Calabrese 1977).

Barium has also been found in sea water at concentrations ranging from 2 to 63 mg/L with a mean concentration of 13 µg/L (Bowen 1979).

5.4.3 Soil

Barium is relatively abundant in the earth's crust and is found in most soils at concentrations ranging from about 15 to 3,000 ppm (Bowen 1979; Schroeder 1970; Shacklette and Boerngen 1984). The barium content in cultivated and uncultivated soil samples collected during a number of field studies ranged from 15 to 1,000 ppm (mean concentration of 300 ppm) for B horizon soils (subsurface soils) in the eastern United States and from 70 to 5,000 ppm (mean concentration of 560 ppm) for B horizon soils in the western United States. Barium content ranged from 150 to 1,500 ppm for surface horizon soils collected in Colorado (mean concentration of 550 ppm) (Connor and Shacklette 1975).

5.4.4 Other Environmental Media

Barium occurs in many foods at low levels. Brazil nuts have notably high concentrations of barium (3,000-4,000 ppm) (Beliles 1979). Some plants bioconcentrate barium from the soil (Beliles 1979; Reeves 1979; Schroeder 1970). The barium content in corn samples from Georgia, Missouri, and Wisconsin collected during a number of field studies ranged from 5 to 150 ppm with mean concentrations ranging from 15 to 54 ppm (Connor and Shacklette 1975). The barium content in other cultivated plants (e.g., lima beans, cabbage, soybeans, and tomatoes) from Georgia, Missouri, and Wisconsin ranged from 7 to 1,500 ppm (mean concentration range: 38-450 ppm) with the highest levels occurring in cabbage from Georgia and soybeans from Missouri and the lowest levels occurring in Georgia tomatoes (Connor and Shacklette 1975).

Barium is also found in anaerobic sewage sludge at concentrations ranging from 100 to 9,000 ppm (mean concentration: 800 ppm) and in aerobic sewage sludge at concentrations ranging from 100 to 300 ppm (mean concentration: 200 ppm) (Sommers 1977).

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5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The primary routes of exposure of humans to barium are consumption of food and water and inhalation of ambient air (ICRP 1974; Reeves 1979). Based on compliance monitoring data from the Federal Reporting Data System (FRDS), of the approximately 214 million people in the United States who are connected to a public water supply, it is estimated that about 150,000 people are exposed to barium concentrations greater than EPA's MCL of 1.0 mg/L (1,000 mg/L) (EPA 1987c). However, since 94% of all samples collected from public water supplies of the 100 largest cities in the United States had barium concentrations of less than 100 mg/L (Durfor and Becker 1964), it is likely that most of the people connected to a public water supply receive drinking water with barium concentrations below the MCL. Assuming an average adult drinking water consumption rate of 1.4 L/day (EPA 1989b) and that barium is present at concentrations of less than 100 mg/L, the average adult daily intake of barium through the consumption of drinking water would be less than 140 mg/day (2 mg/kg/day for a 70-kg adult). Based on an average barium drinking water concentration of 40 mg/L, Hadjimarkos (1967) calculated the average barium intake from drinking water to be about 80 mg/day (1 mg/kg/day for a 70-kg adult). This estimated intake level is consistent with the above estimate of less than 140 mg/day.

The International Commission on Radiological Protection (ICRP 1974) has estimated that intake of barium through inhalation ranges from 0.09 to 26 mg/day. Based on reported urban air concentrations for barium (<0.005 - 1.5 mg/m³) (Tabor and Warren 1958) and assuming an average adult ventilation rate of 20 m³/day (EPA 1989b), the calculated daily respiratory intake of barium ranges from less than 0.1 to 30 mg, which is comparable to the ICRP estimated intake range above. Based on the 8-hour time-weighted average threshold limit value (TLV) in workplace air of 500 µg/m³ (ACGIH 1988), and assuming an 8-hour inhalation of 10 m³ of air, a daily barium workplace intake of 5,000 µg can be calculated. NAS (1977) estimated that 75% of inhaled barium could be absorbed into the bloodstream if soluble barium salts were involved.

Since average ground level concentrations of an emission vary with the distance from the emission point, the population around a source site will be exposed to differing emission levels. Using an average population density of 27 persons/km² (based on actual population data from areas surrounding barium production and processing plants), it has been estimated that approximately 0-886 persons within an area of up to 32.8 km² around a source site could be exposed to soluble barium compound concentrations of greater than 1.67 mg/m³ in ambient air (Reznik and Toy 1978). Assuming that the average adult daily ventilation rate is 20 m³ (EPA 1989b), breathing these ambient air barium concentrations would result in daily respiratory intakes of greater than 32 mg. No other correlations have been established between barium concentrations in air and geographical areas or land-use types.

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Based on consumption of food and beverages in long-term balance studies of four individuals, daily barium intake was estimated to range from 650 to 1,770 mg/day (Tipton et al. 1966, 1969). If an average barium intake of 80 mg/day from drinking water in the United States is assumed (Hadjimarkos 1967), the barium intake from the consumption of non-drinking water dietary sources alone would range from 570 to 1,690 mg/day. Thus, food is typically the primary source of barium exposure for the general population. Gastrointestinal absorption of barium from food is reported to be approximately 6% (ranging from 1% to 15%) (ICRP 1974).

Mean daily balances (excluding loss via hair and sweat) determined from long-term balance studies of four adult subjects ranged from a negative balance of 800 μg to a positive balance of 890 μg (Tipton et al. 1966, 1969). Based on data from these studies, Schroeder (1970) estimated that human daily intake from food (1,160 μg), water (80 μg), and air (10 μg) would be approximately 1,250 μg , and that loss from urine (180 μg), feces (1,010 μg) and other sources (e.g., sweat and hair) (85 μg) would be 1,275 μg . Using these latter estimates of barium intake and loss, a negative barium balance of 25 μg would occur. According to ICRP, the average daily intake of barium from food and fluids (750 μg) and ambient air (0.09-26 μg) ranges from 750 to 776 μg . In addition, ICRP (1974) estimated that approximately 825 μg of barium is lost daily through the urine (50 μg), feces (690 μg), sweat (10 μg), and hair (75 μg). These intake and loss estimates indicate a negative daily balance of up to 75 μg . The day-to-day intake of barium is likely to vary with the quantity and types of food ingested since the barium content in foods varies widely (Schroeder 1970).

In a study of the barium content of the major human organs and tissues, the total body content of barium for a 70-kg adult male was estimated to be about 22,000 μg (ICRP 1974; Schroeder et al. 1972). Ninety-three percent of this barium was found in bone and connective tissue. Large amounts of the remaining 7% existed in fat, skin, and lungs (ICRP 1974; Schroeder et al. 1972).

Occupational exposure to barium primarily occurs in workers and miners who inhale barium sulfate (or the ore, barite) and barium carbonate dust during the mining of barite and the manufacturing and processing (e.g., mixing, grinding, and loading) of barium compounds (Beliles 1979; Reznik and Toy 1978; Schroeder 1970).

Preliminary data from a workplace survey, the National Occupational Exposure Survey (NOES), conducted by NIOSH from 1980 to 1983, estimated the number of workers potentially exposed to various chemicals in the workplace in 1980 (NIOSH 1989), including a separate tally of female workers. The data for barium and barium compounds included in the survey are summarized below:

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<u>Chemical</u>	<u>Number of plants</u>	<u>Total workers (female workers)</u>
Barium	815	10,308 (3,598)
Barium carbonate	4,494	61,019 (6,889)
Barium chloride	4,293	57,767 (15,249)
Barium hydroxide	1,423	35,351 (12,208)
Barium oxide (BaO ₂)	46	511 (325)
Barium nitrate	353	9,625 (2,699)
Barium sulfate	20,089	305,887 (83,800)
Barium sulfide	7	7 (0)
Chromic acid (H ₂ CrO ₄), barium salt (1:1)	20	3,546 (1,984)

The NOES database does not contain information on the frequency, concentration, or duration of exposure of workers to any of the chemicals listed therein. This is a survey that provides only estimates of the number of workers potentially exposed to chemicals in the workplace.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

The general population is commonly exposed to barium primarily through ingestion of drinking water and consumption of food and beverages. However, certain populations face greater than average exposures to this element due to environmental sources, such as drinking water (EPA 1987c). High levels of barium have been reported in groundwater from deep rock and drift wells in several communities in northeastern Illinois (Brenniman et al. 1981; Calabrese 1977) where barium is a naturally occurring geochemical pollutant found almost exclusively in the Cambrian-Ordovician Aquifer (Gilkeson et al. 1978). Other populations that might receive increased exposure to barium are consumers of crops grown on soils that have been used for the land farming of waste oil-well drilling muds (Bates 1988). Individuals who work at or live near barium mining, manufacturing, or processing plants might inhale higher ambient air concentrations or increased amounts of fugitive dust containing barium particulates. Populations living in the vicinity of the 154 NPL sites known to be contaminated with barium may also be exposed to higher than background levels of the compound through contact with contaminated waste site media. No information was found regarding the sizes of these populations or their intake levels of barium.

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA as amended directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of barium is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects

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(and techniques for developing methods to determine such,health effects) of barium.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met, would reduce or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Data Needs

Physical and Chemical Properties. The physical and chemical properties of metallic barium and its inorganic compounds have been well characterized (DOT 1986; EPA 1980a, 1984, 1985c, 1987d; Hawley 1981; Hayes 1982; HSDB 1989; Kirkpatrick 1985; Kunesh 1985; Meister 1989; NIOSH/OSHA 1978; OHM/TADS 1989; Parmeggiani 1983; Perry and Chilton 1973; RTECS 1989; Sax and Lewis 1987, 1989; Sax et al. 1984; Stokinger 1981; Weast 1989; Windholz 1983). Physical and chemical properties of organic compounds of barium have not been comprehensively examined probably due to the limited extent of formation of these compounds. However, further study of the properties of these compounds would help in understanding their role in the environmental fate and transport of barium, particularly at hazardous waste sites where high levels of organic contaminants might be present.

Production, Import/Export, Use, and Disposal. Because barium compounds occur naturally and are widely used in oil well drilling muds, in steel, rubber and plastic products, glass and ceramics, chemical, and pyrotechnics industries, in insecticides, and as a smoke suppressant in diesel fuels (Bodek et al. 1988; EPA 1982; ILO 1983; Kirkpatrick 1985; Meister 1989; Stokinger 1981; Venugopal and Luckey 1978; Worthing 1987), the potential for human exposure to these compounds, such as through ingestion of food and water or inhalation of ambient air, is substantial. However, recent data on production volumes and import and export were not available. In addition, only limited information on disposal of barium compounds was available (HSDB 1989; Joseph 1985; NIOSH/OSHA 1978). Additional information on production, import, export, and disposal would be useful in assessing the potential for the release of, and exposure to, barium 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 the EPA. The Toxic Release Inventory (TRI), which contains this information for 1987, became available in May of 1989. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

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Environmental Fate. The partitioning of barium in environmental media is influenced by the specific form of the compound and such site-specific conditions as pH and cation exchange capacity (Bates 1988; Bodek et al. 1988; Bowen 1966; Kabata-Pendias and Pendias 1984; Lagas et al. 1984). Upon release to the environment, barium is most likely to partition to soils and sediments (Baes et al. 1984; Rai et al. 1984). Barium is transported in the atmosphere, surface waters, soil runoff, and groundwater. In surface waters and soils, barium may ionize and form various salts depending on the pH and the availability of anions (Bates 1988; Bodek et al. 1988; Bowen 1966; Kabata-Pendias and Pendias 1984; Lagas et al. 1984). Additional information on the transport and transformation of barium in the atmosphere would be useful in developing a more complete understanding of the environmental fate of barium compounds.

Bioavailability from Environmental Media. Barium is absorbed following ingestion (Chou and Chin 1943; Cuddihy and Griffith 1972; McCauley and Washington 1983; Taylor et al. 1962) and inhalation (Cuddihy and Ozog 1973b). The bioavailability of barium from air, water, and food has been examined rather extensively in animals (Chou and Chin 1943; Cuddihy and Griffith 1972; McCauley and Washington 1983; Taylor et al. 1962) and humans (Tipton et al. 1969). However, bioavailability from soil has not been studied. Since soil is an important repository for barium, information on barium absorption from ingested soil would be useful in developing an understanding of the potential for exposure following ingestion of contaminated soils, particularly at hazardous waste sites.

Food Chain Bioaccumulation. There is information that barium bioconcentrates in certain plants and aquatic organisms (Bowen 1966; Schroeder 1970). However, the extent to which plants bioconcentrate barium from soil or to which uptake occurs in terrestrial animals is not well characterized. Further studies on the bioconcentration of barium by plants and terrestrial animals and on the biomagnification of barium in terrestrial and aquatic food chains would be useful to better characterize the environmental fate of barium and define the importance of food chain accumulation as a source of human exposure.

Exposure Levels in Environmental Media. Barium has been detected in the atmosphere (Bowen 1979), surface water (Barnett et al. 1969; Bowen 1979; Durfor and Becker 1964; Durum and Haffty 1961; Kopp 1969; Kopp and Kroner 1967; McCabe et al. 1970; Tuovinen et al. 1980), groundwater (Calabrese 1977; Kojola et al. 1970), soils (Bowen 1979; Schroeder 1970; Shacklette and Boerngen 1984), and foodstuffs (Beliles 1979; Connor and Shacklette 1975; Schroeder 1970). There are reliable data to characterize the potential for human exposure via intake of drinking water (Durfor and Becker 1964; Hadjimarkos 1967), and foods (Tipton et al. 1966, 1969); however, the data are not current. Recent data on barium levels in plants and ambient air, soils, and groundwater, particularly from hazardous waste sites, would be useful in

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helping to develop a more complete understanding of the potential for human exposure.

Exposure Levels in Humans. Barium can be detected in blood, urine, feces, and biological tissues (Mauras and Allain 1979; Schramel 1988; Shiraishi et al. 1987). However, there are no data correlating barium levels in tissues and fluids with exposure levels. Additional data are needed on levels of barium in human tissues and fluids following occupational and general population exposure, particularly at hazardous waste sites. This information may be useful in establishing exposure indices for these populations.

Exposure Registries. No exposure registries for barium were located. This compound is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The compound will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to this compound.

5.7.2 On-going Studies

Remedial investigations and feasibility studies conducted at the 154 NPL sites known to be contaminated with barium will add to the available database on exposure levels in environmental media, exposure levels in humans, and exposure registries and will increase the current knowledge regarding the transport and transformation of barium in the environment. No other long-term research studies pertaining to the environmental fate of barium or to occupational or general population exposures to barium were identified.