5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Total chromium has been identified in at least 1,036 and chromium(VI) has been identified in at least 120 of the 1,591 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2000). However, the number of sites evaluated for chromium is not known. The frequency of all these sites can be seen in Figures 5-1 (total chromium) and 5-2 (chromium(VI)). Of the total chromium NPL sites, 1,028 are located within the United States, 7 are located in the Commonwealth of Puerto Rico, and 1 is located in Guam (not shown). Of the chromium(VI) sites, 120 are located within the United States and none are located in the Commonwealth of Puerto Rico or Guam.

Chromium occurs naturally in the Earth's crust. Continental dust is the main source of exposure to natural chromium present in the environment (Fishbein 1981). As a result of human activities, however, chromium is released into the environment in larger amounts. This is indicated by the value of the enrichment factor (ratio of concentration of the element in air to the aluminum concentration in air over the ratio of concentration of the element in the Earth's crust to the aluminum concentration in the Earth's crust) of 3.5–8.1 (Dasch and Wolff 1989; Milford and Davidson 1985). Elements with enrichment factors >1.0 are assumed to have originated from anthropogenic sources (Schroeder et al. 1987). Of the estimated 2,700–2,900 tons of chromium emitted to the atmosphere annually from anthropogenic sources in the United States, . 35% is in the hexavalent form (EPA 1990b). Electroplating, leather tanning, and textile industries release large amounts of chromium to surface waters (Fishbein 1981). Disposal of chromium-containing commercial products and coal ash from electric utilities and other industries are the major sources of chromium release into the soil (Nriagu and Pacyna 1988). Solid waste and slag produced during the roasting and leaching processes of chromium exposure.

Chromium released into the environment from combustion processes and ore processing industries is present mainly as chromium(III) oxide (Cr_2O_3). However, chromium(VI) has been detected in fly ash from coal-fired power plants (Stern et al. 1984) and from chromate manufacturing and user sites. Chromium is primarily removed from the atmosphere by fallout and precipitation. By analogy with copper, the residence time of chromium in the atmosphere is expected to be <10 days (Nriagu 1979). Most of the chromium in lakes and rivers will ultimately be deposited in the sediments. Chromium in the





5. POTENTIAL FOR HUMAN EXPOSURE

284

aquatic phase occurs in the soluble state or as suspended solids adsorbed onto clayish materials, organics, or iron oxides. Most of the soluble chromium is present as chromium(VI) or as soluble chromium(III) complexes and generally accounts for a small percentage of the total. Soluble chromium(VI) may persist in some bodies of water for a long time, but will eventually be reduced to chromium(III) by organic matters or other reducing agents in water (Cary 1982; EPA 1984a). The residence times of chromium (total) in lake water range from 4.6 to 18 years (Schmidt and Andren 1984). Chromium(III) in soil is mostly present as insoluble carbonate and oxide of chromium(III); therefore, it will not be mobile in soil. The solubility of chromium(III) in soil and its mobility may increase due to the formation of soluble complexes with organic matters in soil. A lower soil pH may facilitate complexation. Chromium has a low mobility for translocation from roots to the aboveground parts of plants (Calder 1988; Cary 1982; EPA 1984a, 1985a; King 1988; Stackhouse and Benson 1989).

The arithmetic mean concentrations of total chromium in the ambient air in United States, urban, suburban, and rural areas monitored during 1977–1984 ranged from 0.005 to 0.525 μ g/m³ (EPA 1984a, 1990b). The chromium concentrations in U.S. river waters usually range from <1 to 30 μ g/L, with a median value of 10 μ g/L (Eckel and Jacob 1988; EPA 1984a; Malm et al. 1988; Ramelow et al. 1987; Smith et al. 1987). The total chromium concentrations in U.S. drinking water range from 0.4 to 8.0 μ g/L, with a mean value of 1.8 μ g/L (Greathouse and Craun 1978). In ocean water, the mean chromium concentration is 0.3 μ g/L (Cary 1982). Total chromium concentrations in conterminous U.S. soils range from 1.0 to 2,000 mg/kg, with a mean of 37.0 mg/kg (USGS 1984). The typical chromium levels in most fresh foods are <50 μ g/kg (Fishbein 1984).

The general population is exposed to chromium by eating food or food supplements, drinking water, and inhaling air that contain chromium. The mean daily dietary intake of chromium from air, water, and food is estimated to be <0.2-0.4, 2.0, and $60 \mu g$, respectively (see Section 5.5). Dermal exposure to chromium may also occur during the use of consumer products that contain chromium, such as wood treated with copper dichromate or chromated copper arsenate and leather tanned with chromic sulfate. Exposure to chromium for occupational groups can be two orders of magnitude higher than the exposure to the general population (Hemminki and Vainio 1984). Occupational exposure to chromium occurs mainly from chromate production, stainless steel production and welding, chrome plating, production of ferrochrome alloys, chrome pigment production and user industries, and from working in tanning industries (Stern 1982). Of the general population, people who reside in the vicinity of chromium waste disposal sites and chromium manufacturing and processing plants have a greater probability of elevated chromium exposure.

5.2 RELEASES TO THE ENVIRONMENT

According to the Toxics Release Inventory (TRI), in 1997 a total of 32,811,382 pounds (14,883,243 kg) of chromium was released to the environment from 3,391 large processing facilities (TRI97 1999). Table 5-1 lists estimated amounts released from specific anthropogenic sources during an unspecified time prior to 1990, including the percentage which were in the hexavalent state (EPA 1990b). In addition, an estimated 272,732 pounds (123,711 kg) were released by manufacturing and processing facilities to publicly owned treatment works (POTWs) and an estimated 5,788,705 pounds (2,625,757 kg) were transferred offsite (TRI97 1999). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

5.2.1 Air

According to the Toxics Release Inventory, in 1997 the estimated releases of chromium of 706,204 pounds (320,334 kg) to the air from 3,391 large processing facilities accounted for about 2.2% of total environmental releases (TRI97 1999). Table 5-2 lists amounts released from facilities. 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.

Total chromium has been identified in 45 air samples collected from 1,036 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2000). Chromium(VI) has been identified in 4 air samples collected from 120 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2000).

Continental dust flux is the main natural source of chromium in the atmosphere; volcanic dust and gas flux are minor natural sources of chromium in the atmosphere (Fishbein 1981). Chromium is released into the atmosphere mainly by anthropogenic stationary point sources, including industrial, commercial, and residential fuel combustion, via the combustion of natural gas, oil, and coal. Other important anthropogenic stationary point sources of chromium emission to the atmosphere are metal industries. It has been estimated that . 16,000 metric tons of chromium were emitted into the atmosphere from U.S. anthropogenic sources in 1970 (EPA 1984a). These older estimates indicated that emissions from the metal industry ranged from 35% to 86% of the total, and emissions from fuel combustion ranged from 11% to 65% of the total (EPA 1978). More recent estimates of atmospheric chromium emission in 1976 and 1980 in the Los Angeles, California, and Houston, Texas, areas indicate that emissions from

Source category	Estimated number of sources	Chromium emissions (metric tons/year)	Estimated hexavalent chromium (%)
Combustion of coal and oil	Many	1,723	0.2
Chromium chemical manufacturing	2	18	67
Chemical manufacturing cooling towers	2,039	43	100
Petroleum refining cooling towers	475	32	100
Speciality/steel production	18	103	2.2
Primary metal cooling towers	224	8	100
Chrome plating	4,000	700	. 100
Comfort cooling towers	38,000	7.2–206	100
Texile manufacturing cooling tower	51	0.1	100
Refractory production	10	24	1.3
Ferrochromium production	2	16	5.4
Sewage sludge incineration	133	13	<0.1
Tobacco cooling towers	16	0.2	100
Utility industry cooling towers	6	1.0	100
Chrome ore refining	6	4.8	<0.1
Tire and rubber cooling towers	40	0.2	100
Glass manufacturing cooling towers	3	0.01	100
Cement production	145	3	0.2
Municipal refuse incineration	95	2.5	0.3
NATIONAL TOTAL			2.700-2.900

Table 5-1. Estimates of U.S. Atmospheric Chromium Emissions fromAnthropogenic Sources^a

^aEPA 1990b

		Range of reported amounts released in pounds per year ^a						
State [⊳]	Number of facilities	Air ^c	Water	Land	Underground injection	Total environment ^d	POTW ^e transfer	Off-site waste transfer
AK	1	0	0	0	0	0	0	0
AL	87	24,735	4,043	223,481	0	252,259	907	29,086
AR	49	10,282	557	5,065	0	15,904	1,177	10,450
AZ	31	2,787	0	410,344	0	413,131	653	1,118
CA	147	8,469	1,183	141,237	0	150,889	5,680	31,462
CO	33	2,907	6	1,075	0	3,988	348	10,659
СТ	66	5,573	1,353	5	0	6,931	1,213	39,106
DE	6	3,593	0	2,886	0	6,479	0	0
FL	45	3,035	255	2,790	0	6,080	578	32
GA	90	3,969	10,163	212,648	0	226,780	3,642	125,753
ні	2	0	5	0	0	5	0	0
IA	55	25,163	766	2,747	0	28,676	4,573	2,390
ID	6	2,807	0	733,783	0	736,590	0	0
IL	212	38,165	2,292	1,793,553	0	1,834,010	11,162	666,573
IN	199	68,158	6,341	324,246	2,100	400,845	6,095	22,983
KS	38	17,535	250	108,525	250	126,560	1,381	90,430
KY	72	7,575	721	97,804	0	106100	1,185	58,785
LA	34	17,722	1,129	751	0	19,602	7	5,888

Table 5-2. Releases to the Environment from Facilities that Manufacture or ProcessChromium and Chromium Compounds

		Range of reported amounts released in pounds per year ^a						
State ^b	Number of facilities	Air ^c	Water	Land	Underground injection	Total environment ^d	POTW ^e transfer	Off-site waste transfer
MA	79	3,664	30	1,887	0	5,581	2,267	102,042
MD	32	1,836	1,602	110,605	0	114,043	1,246	23,558
ME	18	910	761	5,217	0	6,888	68,452	202
MI	162	28,689	673	52,956	11,756	94,074	13,373	222,886
MN	49	5,117	24	32	0	5,173	32,210	128
МО	74	28,200	371	10,872	0	39,443	2,285	10,697
MS	49	4,075	1,947	19,219	580,000	605,241	775	18,324
MT	4	505	0	0	0	505	0	0
NC	91	9,630	1,710	9,111,241	0	9,122,581	8,709	19,803
ND	5	97	10	0	0	107	3	0
NE	22	2,094	784	2,505	0	5,383	6,370	38,380
NH	20	5,673	0	0	0	5673	32	1,310
NJ	48	12,069	192	3,600	0	15,861	8,351	36,559
NM	7	1,049	77	330,037	0	331,163	16	5
NV	6	1,282	0	778	0	2,060	0	0
NY	94	18,768	1,810	999,639	0	1,020,217	9,208	40,222
OH	333	118,231	13,385	904,571	250	1036437	9,594	349,302
OK	67	18,491	57	34,788	0	53,336	2,261	5,493

Table 5-2. Releases to the Environment from Facilities that Manufacture or Process Chromium and Chromium Compounds (continued)

		Range of reported amounts released in pounds per year ^a						
State⁵	Number of facilities	Air ^c	Water	Land	Underground injection	Total environment ^d	POTW ^e transfer	Off-site waste transfer
OR	37	6,346	203	13,397	0	19,946	389	14,693
PA	316	10,1742	10,577	156,594	0	268,913	9,383	227,716
PR	4	69	0	0	0	69	0	0
RI	14	18	23	0	0	41	256	250
SC	72	7,823	919	103,254	0	111,996	2,405	20,552
SD	8	80	0	0	0	80	15	250
TN	81	16,101	1,903	79,383	530,000	627,387	1,317	34,512
ТΧ	177	34,582	1,4201	14,598,106	7,203	14,654,092	26,146	3,204,777
UT	28	3,970	250	230,352	0	234,572	1,285	4,698
VA	51	2,007	1,737	2,100	0	5,844	2,667	22,648
VT	4	0	0	4	0	4	255	0
WA	39	4,623	14,426	1,923	0	20,972	389	20,857
WI	197	23,047	1,566	9,993	0	34,606	24,281	158,314
WV	27	2,941	13,082	18,242	0	34,265	191	115,812
WY	3	0	0	0	0	0	0	0
Totals	3,391	706,204	111,384	30,862,235	1,131,559	32,811,382	272,732	5,788,705

Table 5-2. Releases to the Environment from Facilities that Manufacture or Process Chromium and Chromium Compounds (continued)

Source: TRI 97 1999

^aData in TRI are maximum amounts released by each facility

^bPost office state abbreviations used

^cThe sum of fugitive and stack releases are included in releases to air by a given facility

^dThe sum of all releases of the chemical to air, land, and water, and underground injection wells

^ePOTW-Privately-Owned Treatment Works

5. POTENTIAL FOR HUMAN EXPOSURE

stationary fuel combustion are . 46–47% of the total, and emissions from the metal industry range from 26 to 45% of the total (Cass and McRae 1986). The primary stationary nonpoint source of chromium emission into the atmosphere is fugitive emissions from road dusts. Other potentially small sources of atmospheric chromium emission are cement-producing plants (cement contains chromium), the wearing down of asbestos brake linings that contain chromium, incineration of municipal refuse and sewage sludge, and emission from chromium-based automotive catalytic converters. Emissions from cooling towers that previously used chromate chemicals as rust inhibitors are also atmospheric sources of chromium (EPA 1984b; Fishbein 1981).

5.2.2 Water

According to the Toxics Release Inventory, in 1997 the estimated releases of chromium of 111,384 pounds (50,524 kg) to water from 3,391 large processing facilities accounted for about 0.3% of total environmental releases (TRI97 1999). Table 5-2 lists amounts released from facilities. 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.

Total chromium has been identified in 400 surface water and 1,178 groundwater samples collected from 1,036 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2000). Chromium(VI) was identified in 32 surface water and 113 groundwater samples collected from 120 hazardous waste sites where it was detected in some environmental media (HazDat 2000).

The most significant anthropogenic point sources of chromium in surface waters and groundwaters are the waste waters from electroplating operations, leather tanning industries, and textile manufacturing. In addition, deposition of airborne chromium is also a significant nonpoint source of chromium in surface water (Fishbein 1981). In a 1972 survey, the contribution of different sources to chromium load in the influent waste water of a treatment plant in New York City was estimated to be as follows: electroplating industry, 43%; residential waste water, 28%; other industries, 9%; runoff, 9%; and unknown, 11% (Klein et al. 1974). On a worldwide basis, the major chromium source in aquatic ecosystems is domestic waste water effluents (32.2% of the total). The other major sources are metal manufacturing (25.6%), ocean dumping of sewage (13.2%), chemical manufacturing (9.3%), smelting and refining of nonferrous metals (8.1%), and atmospheric fallout (6.4%) (Nriagu and Pacyna 1988). Annual anthropogenic input of chromium into water has been estimated to exceed anthropogenic input into the atmosphere (Nriagu and

Pacyna 1988). However, land erosion, a natural source of chromium in water, was not included in the Nriagu and Pacyna (1988) estimation of chromium contributions to the aquatic environment.

5.2.3 Soil

According to the Toxics Release Inventory, in 1997, the estimated releases of chromium of 30,862,235 pounds (13,999,110 kg) to soil from 3,391 large processing facilities accounted for about 94.1% of total environmental releases (TRI97 1999). An additional 1,131,559 pounds (513,275 kg) of chromium, amounting to 3.4% of the total environmental release, was injected underground. Table 5-2 lists the amounts released from facilities. 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.

Total chromium has been identified in 939 soil and 472 sediment samples collected from 1,036 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2000). Chromium(VI) has been identified in 59 soil and 22 sediment samples collected from 120 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2000).

On a worldwide basis, the disposal of commercial products that contain chromium may be the largest contributor, accounting for . 51% of the total chromium released to soil (Nriagu and Pacyna 1988). Other significant sources of chromium release into soil include the disposal of coal fly ash and bottom fly ash from electric utilities and other industries (33.1%), agricultural and food wastes (5.3%), animal wastes (3.9%), and atmospheric fallout (2.4%) (Nriagu and Pacyna 1988). Solid wastes from metal manufacturing constituted <0.2% to the overall chromium release in soil. However, the amount of chromium in sludge or residue that is disposed of in landfills by manufacturing and user industries that treat chromate wastes in ponds and lagoons is not included in the estimation by Nriagu and Pacyna (1988).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Chromium is present in the atmosphere primarily in particulate form. Naturally occurring gaseous forms of chromium are rare (Cary 1982). The transport and partitioning of particulate matter in the atmosphere depend largely on particle size and density. Atmospheric particulate matter is deposited on land and

5. POTENTIAL FOR HUMAN EXPOSURE

water via wet and dry deposition. In the case of chromium, the mass median diameter of the ambient atmospheric particle is . 1 μ m (Milford and Davidson 1985; Ondov et al. 1989), and the deposition velocity is 0.5 cm/second (Schroeder et al. 1987). This size and deposition velocity favor dry deposition by inertial impaction (Schroeder et al. 1987). Wet removal of particulate chromium also occurs by rainout within a cloud, and washout below a cloud, and acid rain may facilitate removal of acid-soluble chromium compounds from the atmosphere. The wet scavenging ratio (i.e., the concentration of contaminant in precipitation over the concentration in unscavenged air) ranges from 150 to 290 for chromium (Dasch and Wolff 1989; Schroeder et al. 1987). The wet deposition ratio increases with particle size and decreases with precipitation intensity (Schroeder et al. 1987). Chromium particles of aerodynamic diameter <20 μ m may remain airborne for longer periods of time and be transported for greater distances than larger particles. The monthly dry deposition flux rate of chromium measured in Bologna, Italy over the course of one year ranged from about 40–270 μ g/m²-month with the largest values occurring during the winter months (Morselli et al. 1999).

A maximum of 47% of the total chromium in ferrochrome smelter dust may be bioavailable as indicated by acid/base extraction. About 40% of the bioavailable chromium may exist as chromium(VI), mostly in the form of $Cr_2O_7^{-2}$ or CrO_4^{-2} (Cox et al. 1985). There are no data in the reviewed literature indicating that chromium particles are transported from the troposphere to the stratosphere (Pacyna and Ottar 1985). By analogy with the residence time of general particles with mass median diameters similar to that of chromium, the residence time of atmospheric chromium is expected to be <10 days (Nriagu 1979). Based on a troposphere to stratosphere turnover time of 30 years (EPA 1979), atmospheric particles with a residence time of <10 days are not expected to transport from the troposphere to the stratosphere.

Since chromium compounds cannot volatilize from water, transport of chromium from water to the atmosphere is not likely, except by transport in windblown sea sprays. Most of the chromium released into water will ultimately be deposited in the sediment. A very small percentage of chromium can be present in water in both soluble and insoluble forms. Soluble chromium generally accounts for a very small percentage of the total chromium. Most of the soluble chromium is present as chromium(VI) and soluble chromium(III) complexes. Less than 0.002% of total chromium in water and sediment in the Amazon and Yukon Rivers was present in a soluble form (Cary 1982). In the aquatic phase, chromium(III) occurs mostly as suspended solids adsorbed onto clayish materials, organics, or iron oxide (Fe₂O₃) present in water. Approximately 10.5–12.6% of chromium in the aquatic phase of the Amazon and Yukon rivers was in solution, the rest being present in the suspended solid phase (Cary 1982; King 1988). The ratio of suspended to dissolved solid in an organic-rich river in Brazil was 2.1 (Malm et al.

5. POTENTIAL FOR HUMAN EXPOSURE

1988). Soluble forms and suspended chromium can undergo intramedia transport. Chromium(VI) in water will eventually be reduced to chromium(III) by organic matter in the water. It has been estimated that the residence time of chromium (total) in Lake Michigan ranges from 4.6 to 18 years (Fishbein 1981; Schmidt and Andren 1984).

The bioconcentration factor (BCF) for chromium(VI) in rainbow trout (*Salmo gairdneri*) is 1. In bottomfeeder bivalves, such as the oyster (*Crassostrea virginica*), blue mussel (*Mytilus edulis*), and soft shell clam (*Mya arenaria*), the BCF values for chromium(III) and chromium(VI) may range from 86 to 192 (EPA 1980, 1984a; Fishbein 1981; Schmidt and Andren 1984). The bioavailability of chromium(III) to freshwater invertebrates (*Daphnia pulex*) decreased with the addition of humic acid (Ramelow et al. 1989). This decrease in bioavailability was attributed to lower availability of the free form of the metal due to its complexation with humic acid. Based on this information, chromium is not expected to biomagnify in the aquatic food chain. Although higher concentrations of chromium have been reported in plants growing in high chromium-containing soils (e.g., soil near ore deposits or chromium-emitting industries and soil fertilized by sewage sludge) compared with plants growing in normal soils, most of the increased uptake in plants is retained in roots, and only a small fraction is translocated in the aboveground part of edible plants (Cary 1982; WHO 1988). Therefore, bioaccumulation of chromium from soil to above-ground parts of plants is unlikely (Petruzzelli et al. 1987). There is no indication of biomagnification of chromium along the terrestrial food chain (soil-plant-animal) (Cary 1982).

Chromium in soil is present mainly as insoluble oxide $Cr_2O_3 \mathfrak{B}H_2O$ (EPA 1984a), and is not very mobile in soil. A leachability study was conducted to study the mobility of chromium in soil. Due to different pH values, a complicated adsorption process was observed and chromium moved only slightly in soil. Chromium was not found in the leachate from soil, possibly because it formed complexes with organic matter. These results support previous data finding that chromium is not very mobile in soil (Lin et al. 1996). These results are supported by leachability investigation in which chromium mobility was studied for a period of 4 years in a sandy loam (Sheppard and Thibault 1991). The vertical migration pattern of chromium in this soil indicated that after an initial period of mobility, chromium forms insoluble complexes and little leaching is observed. Flooding of soils and the subsequent anaerobic decomposition of plant detritus matters may increase the mobilization of chromium(III) in soils due to formation of soluble complexes (Stackhouse and Benson 1989). This complexation may be facilitated by a lower soil pH. A smaller percentage of total chromium in soil exists as soluble chromium(VI) and chromium(III), which are more mobile in soil. The mobility of soluble chromium in soil will depend on the sorption characteristics of the soil. The relative retention of metals by soil is in the order of lead > antimony >

copper > chromium > zinc > nickel > cobalt > cadmium (King 1988). The sorption of chromium to soil depends primarily on the clay content of the soil and, to a lesser extent, on Fe_2O_3 and the organic content of soil. Chromium that is irreversibly sorbed onto soil, for example, in the interstitial lattice of geothite, FeOOH, will not be bioavailable to plants and animals under any condition. Organic matter in soil is expected to convert soluble chromate, chromium(VI), to insoluble chromium(III) oxide, Cr_2O_3 (Calder 1988). Chromium in soil may be transported to the atmosphere as an aerosol. Surface runoff from soil can transport both soluble and bulk precipitate of chromium to surface water. Soluble and unadsorbed chromium(VI) and chromium(III) complexes in soil may leach into groundwater. The leachability of chromium(VI) in the soil increases as the pH of the soil increases. On the other hand, lower pH present in acid rain may facilitate leaching of acid-soluble chromium(III) and chromium(VI) compounds in soil. Chromium has a low mobility for translocation from roots to aboveground parts of plants (Cary 1982). However, depending on the geographical areas where the plants are grown, the concentration of chromium in aerial parts of certain plants may differ by a factor of 2–3 (Cary 1982).

5.3.2 Transformation and Degradation

5.3.2.1 Air

In the atmosphere, chromium(VI) may be reduced to chromium(III) at a significant rate by vanadium $(V^{2+}, V^{3+}, and VO^{2+})$, Fe²⁺, HSO³⁻, and As³⁺ (EPA 1987b). Conversely, chromium(III), if present as a salt other than Cr₂O₃, may be oxidized to chromium(VI) in the atmosphere in the presence of at least 1% manganese oxide (EPA 1990b). However, this reaction is unlikely under most environmental conditions (see Section 5.3.2.2). The estimated atmospheric half-life for chromium(VI) reduction to chromium(III) was reported in the range of 16 hours to about 5 days (Kimbrough et al. 1999).

5.3.2.2 Water

The reduction of chromium(VI) and the oxidation of chromium(III) in water has been investigated. The reduction of chromium(VI) by S^{-2} or Fe^{+2} ions under anaerobic conditions was fast, and the reduction half-life ranged from instantaneous to a few days. However, the reduction of chromium(VI) by organic sediments and soils was much slower and depended on the type and amount of organic material and on the redox condition of the water. The reaction was generally faster under anaerobic than aerobic conditions. The reduction half-life of chromium(VI) in water with soil and sediment ranged from 4 to 140 days (Saleh et al. 1989). Dissolved oxygen by itself in natural waters did not cause any measurable

5. POTENTIAL FOR HUMAN EXPOSURE

oxidation of chromium(III) to chromium(VI) in 128 days (Saleh et al. 1989). When chromium(III) was added to lake water, a slow oxidation of chromium(III) to chromium(VI) occurred, corresponding to an oxidation half-life of nine years. Addition of 50 mg/L manganese oxide accelerated the process, decreasing the oxidation half-life to . 2 years (Saleh et al. 1989). Therefore, this oxidation process would not be significant in most natural waters. The oxidation of chromium(III) to chromium(VI) during chlorination of water was highest in the pH range of 5.5–6.0 (Saleh et al. 1989). However, the process would rarely occur during chlorination of drinking water because of the low concentrations of chromium(III) in these waters, and the presence of naturally occurring organics that may protect chromium(III) from oxidation, either by forming strong complexes with chromium(III) or by acting as a reducing agent to free available chlorine (EPA 1988c). In chromium(III) to chromium(VI) in the absence of having pH ranges of 5–7, chlorination may convert chromium(III) to chromium(VI) in the absence of

Chromium speciation in groundwater depends on the redox potential and pH conditions in the aquifer. Chromium(VI) predominates under highly oxidizing conditions; whereas chromium(III) predominates under reducing conditions. Oxidizing conditions are generally found in shallow aquifers, and reducing conditions generally exist in deeper groundwaters. In sea water, chromium(VI) is generally stable (Fukai 1967). In natural groundwater, the pH is typically 6–8, and CrO_4^{-2} is the predominant species of chromium in the hexavalent oxidation state, while $Cr(OH)_2^{+1}$ will be the dominant species in the trivalent oxidation state. This species and other chromium(III) species will predominate in more acidic pH; $Cr(OH)_3$ and $Cr(OH)_4^{-1}$ predominate in more alkaline waters (Calder 1988).

chromium(III)-complexing and free chlorine reducing agents (EPA 1988c).

5.3.2.3 Sediment and Soil

The fate of chromium in soil is greatly dependent upon the speciation of chromium, which is a function of redox potential and the pH of the soil. In most soils, chromium will be present predominantly in the chromium(III) state. This form has very low solubility and low reactivity resulting in low mobility in the environment and low toxicity in living organisms (Barnhart 1997). Under oxidizing conditions chromium(VI) may be present in soil as CrO_4^{-2} and $HCrO_4^{-1}$ (James et al. 1997). In this form, chromium is relatively soluble, mobile, and toxic to living organisms. In deeper soil where anaerobic conditions exist, chromium(VI) will be reduced to chromium(III) by S⁻² and Fe⁺² present in soil. The reduction of chromium(VI) to chromium(III) is possible in aerobic soils that contain appropriate organic energy sources to carry out the redox reaction. The reduction of chromium(VI) to chromium(III) is facilitated by low pH (Cary 1982; EPA 1990b; Saleh et al. 1989). From thermodynamic considerations, chromium(VI)

5. POTENTIAL FOR HUMAN EXPOSURE

may exist in the aerobic zone of some natural soil. The oxidation of chromium(III) to chromium(VI) in soil is facilitated by the presence of low oxidizable organic substances, oxygen, manganese dioxide, and moisture. Oxidation is also enhanced at elevated temperatures in surface soil that result from brush fires (Calder 1988; Cary 1982). Organic forms of chromium(III) (e.g., humic acid complexes) are more easily oxidized than insoluble oxides. However, oxidation of chromium(III) to chromium(VI) was not observed in soil under conditions of maximum aeration and a maximum pH of 7.3 (Bartlett and Kimble 1976). It was later reported that soluble chromium(III) in soil can be partly oxidized to chromium(VI) by manganese dioxide in soil, and the process is enhanced by pH higher than six (Bartlett 1991). Because most chromium(III) in soil is immobilized due to adsorption and complexation with soil materials, the barrier to this oxidation process is the lack of availability of mobile chromium(III) to immobile manganese dioxide in soil surfaces. Due to this lack of availability of mobile chromium(III) to manganese dioxide surfaces, a large portion of chromium in soil will not be oxidized to chromium(VI), even in the presence of manganese dioxide and favorable pH conditions (Bartlett 1991; James et al. 1997).

The microbial reduction of chromium(VI) to chromium(III) has been discussed as a possible remediation technique in heavily contaminated environmental media or wastes (Chen and Hao 1998). Factors affecting the microbial reduction of chromium(VI) to chromium(III) include biomass concentration, initial chromium(VI) concentration, temperature, pH, carbon source, oxidation-reduction potential and the presence of both oxyanions and metal cations. Although high levels of chromium(VI) are toxic to most microbes, several resistant bacterial species have been identified which could ultimately be employed in remediation strategies (Chen and Hao 1998). Elemental iron, sodium sulfite, sodium hydrosulfite, sodium bisulfite, sodium metabisulfite sulfur dioxide and certain organic compounds such as hydroquinone have also been shown to reduce chromium(VI) to chromium(III) and have been discussed as possible remediation techniques in heavily contaminated soils (James et al. 1997; Higgins et al. 1997). The limitations and efficacy of these and all remediation techniques are dependent upon the ease in which the reducing agents are incorporated into the contaminated soils.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to chromium depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing data on chromium levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

5.4.1 Air

The atmospheric total chromium concentration in the United States is typically <10 ng/m³ in rural areas and 10-30 ng/m³ in urban areas (Fishbein 1984). Levels of total chromium in the ambient air in U.S. urban and nonurban areas during 1977–1984 are reported in EPA (1990b). Levels of total chromium in the ambient air in U.S. urban and nonurban areas during 1977–1984 are reported in EPA's National Aerometric Data Bank (EPA 1984a, 1990b). According to this databank, the arithmetic mean total chromium concentrations from a total of 2,106 monitoring stations ranged from 5 to 525 ng/m^3 . The two locations that showed the highest total arithmetic mean chromium concentrations were in Steubenville, Ohio, in 1977 (525 ng/m³) and in Baltimore, Maryland, in 1980 (226 ng/m³) (EPA 1990b). Arithmetic mean total chromium concentrations in only 8 of 173 sites monitored in 1984 were >100 ng/m³ (EPA 1990b). An indoor/outdoor air study was conducted in southwestern Ontario to measure levels of chromium(VI) and the size fraction of chromium(VI). Indoor and outdoor samples were taken from 57 homes during the summer months of 1993. The concentrations were 0.1-0.6 ng/m³ indoors (geometric mean 0.2 ng/m^3) and were 0.10–1.6 ng/m^3 outdoors (geometric mean 0.55 ng/m^3). The indoor concentrations were less than ¹/₂ of the outdoor concentrations. Analysis of airborne chromium(VI) particles showed that they are inhalable in size (Bell and Hipfner 1997). During the period 1978–1982, The maximum level of total chromium in ambient air samples in Corpus Christi, Texas, a site of chromate manufacture, was 5,500 ng/m³. The annual average concentration of chromium in Corpus Christi ambient air was 400 ng/m³ during the same period (Wiersema 1984). The EPA monitored two locations in Corpus Christi in 1981 and reported an arithmetic mean chromium concentration of 100 ng/m³ (EPA 1990b). A recent study measured the levels of chromium(VI) and total chromium in the ambient air. The concentrations of chromium(VI) in the indoor air of residences in Hudson County, New Jersey, in 1990 ranged from 0.38 to 3,000 ng/m³, with a mean of 1.2 ng/m³ (Falerios et al. 1992). An indoor/outdoor study was conducted at 25 industrial sites in Hudson County. New Jersey to analyze soils containing chromite ore processing residues. The industrial sites include industrial, manufacturing, trucking, and warehouse facilities. The study found industrial indoor chromium(VI) and total chromium concentrations to be 0.23-11 ng/m³ and 4.1-130 ng/m³ and industrial outdoor chromium(VI) and total chromium concentrations to be 0.013–15.3 ng/m³ and 1.9–84.5 ng/m³. The results of this study found that higher levels of chromium(VI) in soil do not result in higher levels of chromium(VI) in air (Finley et al. 1993). The mean concentration of total chromium at the same sites was 7.1 ng/m^3 , with a concentration range of 3.7–12 ng/m³. Recent monitoring data in Hudson County, NJ has shown a background chromium(VI) concentration of 0.2 to 3.8 ng/m³ with a mean concentration of 1.2 ng/m³ (Scott et al. 1997a). The airborne total chromium concentration range was 1.5-10 ng/m³ with a mean concentration of 4.5 ng/m³

298

(Scott et al. 1997a). The mean airborne chromium(VI) and total chromium concentrations in the indoor air of industrial sites in Hudson County, New Jersey, contaminated by chromite ore-processing residue were 3 ng/m³ (range, 0.23–11 ng/m³) and 23 ng/m³ (range, 4.11–130 ng/m³), respectively. The mean airborne chromium(VI) and total chromium concentrations in outdoor air for the same sites were 9.9 ng/m³ (range, 0.13–110 ng/m³) and 37 ng/m³ (range, 1.9–250 ng/m³), respectively (Falerios et al. 1992). An air dispersion model was recently developed which accurately estimated chromium(VI) concentrations at two of these industrial sites in Hudson County, NJ (Scott et al. 1997b). The background corrected airborne concentrations in ng/m³ for seven sampling dates are reported as measured (estimated): 0.0 (0.41); 6.2 (7.7); 0.9 (1.7); 2.8 (2.7); 0.0 (0.08); 0.3 (0.1); and 1.2 (0.12). The estimated percent levels of chromium(III) and chromium(VI) in the U.S. atmosphere from anthropogenic sources are given in Table 5-1 (EPA 1990b). Fly ash from a coal-fired power plant contained 1.4–6.1 mg/kg chromium(VI) (Stern et al. 1984). In a field study to assess inhalation exposure to chromium during showering and bathing activities, the average chromium(VI) concentration in airborne aerosols ranged from 87 to 324 ng/m³ when water concentrations of 0.89–11.5 mg/L of chromium(VI) were used in a standard house shower (Finley et al. 1996a).

The concentrations of atmospheric chromium in remote areas range from 0.005 to 2.6 ng/m³ (Barrie and Hoff 1985; Cary 1982; Schroeder et al. 1987; Sheridan and Zoller 1989). Saltzman et al. (1985) compared the levels of atmospheric chromium at 59 sites in U.S. cities during 1968–1971 with data from EPA's National Aerometric Data Bank file for 1975–1983. They concluded that atmospheric chromium levels may have declined in the early 1980s from the levels detected in the 1960s and 1970s.

5.4.2 Water

Chromium concentrations in U.S. river water usually range from <1 to 30 μ g/L (EPA 1984a; Malm et al. 1988; Ramelow et al. 1987), with a median value of 10 μ g/L (Eckel and Jacob 1988; Smith et al. 1987). Chromium concentrations in lake water generally do not exceed 5 μ g/L (Borg 1987; Cary 1982). The higher levels of chromium can be related to source(s) of anthropogenic pollution. Dissolved chromium concentrations of 0.57–1.30 μ g/L were reported in the Delaware River near Marcus Hook and Fieldsboro, Pennsylvania in January 1992, with chromium(III) composing 67% of the total (Riedel and Sanders 1998). In March 1992 these concentrations decreased to 0.03–0.23 μ g/L. The chromium levels detected in drinking water in an earlier study (1962–1967 survey) may be erroneous due to questionable sampling and analytical methods (see Section 6.1) (EPA 1984a). A survey conducted from 1974 to 1975 that had a detection limit of 0.1 μ g/L and surveyed 3,834 U.S. tap waters probably provides better estimates of

5. POTENTIAL FOR HUMAN EXPOSURE

299

chromium concentrations in U.S. drinking water. The survey reported chromium concentrations in drinking water that ranged from 0.4 to 8.0 μ g/L, with a mean value of 1.8 μ g/L (Greathouse and Craun 1978). These values may be higher than the actual values, due to inadequate flushing of tap water before sample collection (EPA 1984a). The concentration of chromium in household tap water may be higher than supply water due to corrosion of chromium-containing pipes. At a point of maximum contribution from corrosion of the plumbing system, the peak chromium in tap water in Boston, Massachusetts, was $15 \mu g/L$ (Ohanian 1986). A survey that targeted drinking waters from 115 Canadian municipalities during 1976–1977 reported the median and the range of chromium concentrations to be $<2.0 \ \mu g/L$ (detection limit) and $\leq 2.0-8.0 \ \mu g/L$, respectively (Meranger et al. 1979). The mean chromium concentration in ocean water is 0.3 μ g/L, with a range of 0.2–50 μ g/L (Cary 1982). In general, the concentration of chromium in ocean water is much lower than that in lakes and rivers. The concentrations of total chromium in groundwater at the Idaho National Engineering Laboratory, where chromate is used as a corrosion inhibitor, ranged from ≤ 1 to 280 µg/L (USGS 1989). The water from a village well situated near a waste pond receiving chromate waste in Douglas, Michigan, contained 10,800 µg/L chromium(VI). Similarly, water from a private well adjacent to an aircraft plant in Nassau County, New York, contained 25,000 µg/L chromium(VI), while water from a public well adjacent to another aircraft plant in Bethpage, New York, contained 1,400 µg/L (chromium(VI) (Davids and Lieber 1951). In a later study, water from an uncontaminated well in Nassau County, New York, contained an undetectable level of chromium(VI), whereas a contaminated well in the vicinity of a plating plant contained $6,000 \mu g/L$ chromium(VI) (Lieber et al. 1964). A high chromium concentration (120 µg/L) was detected in private drinking water wells adjacent to a NPL site in Galena, Kansas (ATSDR 1990a). The mean concentration of chromium in rainwater is 0.14–0.9 µg/L (Barrie et al. 1987; Dasch and Wolff 1989).

5.4.3 Sediment and Soil

The chromium level in soils varies greatly and depends on the composition of the parent rock from which the soils were formed. Basalt and serpentine soils, ultramafic rocks, and phosphorites may contain chromium as high as a few thousand mg/kg (Merian 1984) whereas soils derived from granite or sandstone will have lower concentrations of chromium (Swaine and Mitchell 1960). The concentration range of chromium in 1,319 samples of soils and other surficial materials collected in the conterminous United States was 1–2,000 mg/kg, with a geometric mean of 37 mg/kg (USGS 1984). Chromium concentrations in Canadian soils ranged from 5 to 1,500 mg/kg, with a mean of 43 mg/kg (Cary 1982). In a study with different kinds of soils from 20 diverse sites including old chromite mining sites in Maryland, Pennsylvania, and Virginia, the chromium concentration ranged from 4.9 to 71 mg/kg (Beyer

5. POTENTIAL FOR HUMAN EXPOSURE

and Cromartie 1987). A polynuclear aromatic hydrocarbon (PAH) soil study was conducted to determine the metal levels in soil at the edge of a busy road that runs through the Aplerbecker Forest in West Germany. Chromium(VI) concentrations of 64 mg/kg were measured, and these concentrations were 2to 4-fold higher along the road than in the natural forest (Munch 1993). The soil beneath decks treated with chrominated copper arsenate (CCA), a wood preservative, had an average chromium content of 43 mg/kg (Stilwell and Gorny 1997).

Chromium has been detected at a high concentration (43,000 mg/kg) in soil at the Butterworth Landfill site in Grand Rapid City, Michigan, which was a site listed on the NPL (ATSDR 1990b).

Chromium was detected in sediment obtained from the coastal waters of the eastern U.S. seashore at concentrations of $3.8-130.9 \ \mu g/g$ in 1994 and $0.8-98.1 \ \mu g/g$ in 1995 (Hyland et al. 1998).

5.4.4 Other Environmental Media

The concentration of chromium in the particulate portion of melted snow collected from two urban areas (Toronto and Montreal) of Canada ranged from 100 to 3,500 mg/kg (Landsberger et al. 1983). In the suspended materials and sediment of water bodies, chromium levels ranged from 1 to 500 mg/kg (Byrne and DeLeon 1986; EPA 1984a; Mudroch et al. 1988; Ramelow et al. 1987). The chromium concentration in incinerated sewage sludge ash may be as high as 5,280 mg/kg (EPA 1984a).

Total chromium levels in most fresh foods are extremely low (vegetables (20–50 μ g/kg), fruits (20 μ g/kg), and grains and cereals (40 μ g/kg)) (Fishbein 1984). The chromium levels of various foods are reported in Table 5-3. In a study to find the concentrations of chromium in edible vegetables in Tarragon Province, Spain, the highest levels of chromium were found in radish root and spinach, with a non-significant difference between the samples collected in two areas (northern industrial and southern agricultural). The samples ranged in concentration from 0.01 μ g/g to 0.21 μ g/g (industrial) and from 0.01 μ g/g to 0.22 μ g/g (agricultural) (Schuhmaker et al. 1993). Acidic foods that come into contact with stainless steel surfaces during harvesting, processing, or preparation for market are sometimes higher in chromium from foods (e.g., whole-grain bread contains 1,750 μ g/kg chromium, but processed white bread contains only 140 μ g/kg; and molasses contains 260 μ g/kg chromium, but refined sugar contains only 20 μ g/kg chromium) (Anderson 1981; EPA 1984a).

Sample	Mean concentration (µg/kg)	Reference
Fresh vegetables	30–140	EPA 1984a
Frozen vegetables	230	EPA 1984a
Canned vegetables	230	EPA 1984a
Fresh fruits	90–190	EPA 1984a
Fruits	20	EPA 1984a
Canned fruits	510	EPA 1984a
Dairy products	100	EPA 1984a
Chicken eggs	160–520	Kirpatrick and Coffin 1975
Chicken eggs	60	Kirpatrick and Coffin 1975
Whole fish	50–80	EPA 1984a
Edible portion of fresh fin fish	<100–160	Eisenberg and Topping 1986
Meat and fish	110–230	EPA 1984a
Seafoods	120–470	EPA 1984a
Grains and cereals	40–220	EPA 1984a
Sugar, refined ^a	<20	WHO 1988

Table 5-3. Chromium Content in Various U.S. Foods

^aValue in Finnish sugar

5. POTENTIAL FOR HUMAN EXPOSURE

Chromium levels in oysters, mussels, clams, and mollusks vary from <0.1 to 6.8 mg/kg (dry weight) (Byrne and DeLeon 1986; Ramelow et al. 1989). Fish and shellfish collected from ocean dump sites off New York City, Delaware Bay, and New Haven, Connecticut, contained <0.3–2.7 mg/kg chromium (wet weight) (Greig and Jones 1976). The chromium concentration in fish sampled from 167 lakes in the northeastern United States was 0.03–1.46 μ g/g with a mean concentration of 0.19 μ g/g (Yeardley et al. 1998). Higher levels of chromium in forage of meat animals have been reported for plants grown in soils with a high concentration of chromium (see Section 5.3.1). Cigarette tobacco reportedly contains 0.24–14.6 mg/kg chromium, but no estimates were available regarding the chromium levels in inhaled cigarette smoke (Langård and Norseth 1986). Cigarette tobacco grown in the United States contains #6.3 mg/kg chromium (IARC 1980).

Cement-producing plants are a potential source of atmospheric chromium. Portland cement contains 41.2 mg/kg chromium (range 27.5–60 mg/kg). Soluble chromium accounts for 4.1 mg/kg (range 1.6–8.8 mg/kg) of which 2.9 mg/kg (range 0.03–7.8 mg/kg) is chromium(VI) (Fishbein 1981). The wearing down of vehicular brake linings that contain asbestos represents another source of atmospheric chromium. Asbestos may contain . 1,500 mg/kg of chromium. The introduction of catalytic converters on U.S. automobiles in 1975 in the United States represented an additional source of atmospheric chromium. Catalysts, such as copper chromite, emit $<10^6$ metal-containing condensation nuclei per cubic centimeter in vehicular exhaust, under various operating conditions (Fishbein 1981).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The general population is exposed to chromium by inhaling ambient air, ingesting food, and drinking water containing chromium. Dermal exposure of the general public to chromium can occur from skin contact with certain consumer products that contain chromium. Some of the consumer products known to contain chromium are certain wood preservatives, cement, cleaning materials, textiles, and leather tanned with chromium (WHO 1988). However, no quantitative data for dermal exposure to chromium-containing consumer products were located. Levels of chromium in ambient air (<0.01–0.03 μ g/m³) (Fishbein 1984) and tap water (<2 μ g/L) (Greathouse and Craun 1979) have been used to estimate the daily intake of chromium via inhalation (<0.2–0.6 μ g) and via tap water (<4 μ g). These estimates are based on an air inhalation rate of 20 m³/day and a drinking water consumption rate of 2 L/day. The daily chromium intake for the U.S. population from consumption of selected diets (diets with 25 and 43% fat) has been estimated to range from 25 to 224 μ g with an average of 76 μ g (Kumpulainen et al. 1979). The average value is close to a value of 60 μ g reported by Bennett (1986). The bioavailability of chromium

5. POTENTIAL FOR HUMAN EXPOSURE

from different foods may vary. No correlation was found between the insulin potentiation and the total chromium extractable from foods by acid hydrolysis. However, a significant correlation was found between the ethanol-extractable chromium and biological activity. The highest amounts of ethanol-extractable chromium were found in brewer's yeast, black pepper, calf-liver, cheese, and wheatgerm (WHO 1988). The chromium concentrations in tissues and body fluids of the general population are given in Table 5-4.

Workers in industries that use chromium can be exposed to concentrations of chromium two orders of magnitude higher than exposure to the general population (Hemminki and Vainio 1984). Occupational exposure to chromium occurs mainly from chromate production, stainless steel production and welding, chromium plating, ferrochrome alloys and chrome pigment production, and working in tanning industries. A list of industries that may be sources of chromium exposure is given in Table 5-5. For most occupations, exposure is due to both chromium(III) and chromium(VI) present as soluble and insoluble fractions. However, exceptions include: the tanning industry, where exposure is mostly from soluble chromium(III) and the plating industry, where exposure is due to soluble chromium(VI). The typical concentration ranges of airborne chromium(VI) to which workers in these industries were exposed during an average of 5-20 years of employment were: chromate production, $100-500 \text{ µg/m}^3$; stainless steel welding, $50-400 \ \mu g/m^3$; chromium plating, $5-25 \ \mu g/m^3$; ferrochrome alloys, $10-140 \ \mu g/m^3$; and chrome pigment, $60-600 \text{ µg/m}^3$ (Stern 1982). In the tanning industry, except for 2 bath processes, the typical exposure range due to chromium(III) was 10–50 μ g/m³. A more recent study of chromium oxide levels in the working environment of stainless steel welders in Germany reported a maximum value of 80 µg/m³, with a median value ranging from 4 to 10 μ g/m³ (Angerer et al. 1987). Because of better emission control measures, occupational airborne chromium concentrations have declined significantly since the 1970s (Stern 1982). In a recent study conducted in Taiwan to estimate worker exposure to chromium in electroplating factories, the chromium concentrations were $0.5-6.0 \text{ µg/m}^3$ near the electroplating tanks and 0.3 µg/m^3 in the manufacturing area (Kuo et al. 1997b). In an occupational exposure study of chromium in an aircraft construction factory, airborne samples were collected over a 4-hour period; urinary samples were collected at the beginning (Monday), end (Friday), and after the work shift in order to analyze the absorption of chromium during working hours (Gianello et al. 1998). The air sampling results were 0.02-1.5 mg/m³, and the urine sampling results were $0.16-7.74 \,\mu g/g$ creatinine. Compared to the ACGIH and BEI-ACGIH Hygiene Standard of 50 μ g/m³, both sets of results indicated a very low risk of exposure. The National Occupational Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983 estimated that 304,829 workers in the United States were potentially exposed to chromium(VI) (NIOSH 1989). The NOES database does not contain information on the frequency, concentration, or

Sample	Median/mean	Range	Reference
Serum	0.006 µg/L	0.01–0.17 μg/L	Sunderman et al. 1987
Urine	0.4 μg/L	0.24–1.8 µg/L	lyengar and Woittiez 1988
Lung	201 µg/kg (wet weight)	28–898 µg/kg (wet weight)	Raithel et al. 1987
Breast milk	0.30 µg/L	0.06–1.56 μg/L	Casey and Hambidge 1984
Hair	0.234 mg/kg	Not available	Takagi et al. 1986
Nail	0.52 mg/kg	No applicable	Takagi et al. 1988

Table 5-4. Chromium Content in Tissues and Body Fluids of the GeneralPopulation

Table 5-5.	Industries	that May be	Sources of	Chromium	Exposure ^a
		·····			

Abrasives manufacturers Acetylene purifiers Adhesives workers Aircraft sprayers Alizarin manufacturers Alloy manufactures Aluminum anodizers Anodizers Battery manufacturers Biologists Blueprint manufacturers Boiler scalers Candle manufacturers Cement workers Ceramic workers Chemical workers Chromate workers Chromium-alloy workers Chromium-alloy workers Chromium-alloy workers Chromium-allers Copper etchers Copper etchers Copper etchers Copper-plate strippers Corrosion-inhibitor workers Crayon manufacturers Diesel locomotive repairmen Drug manufacturers Dyers Electroplaters Enamel workers Explosive manufacturers Fat purifiers Fireworks manufacturers Flypaper manufacturers Furniture polishers Furniture polishers Fur processors Glass-fibre manufacturers	Laboratory workers Leather finishers Linoleum workers Lithographers Magnesium treaters Match manufacturers Metal cleaners Metal workers Milk preservers Oil drillers Oil purifiers Painters Palm-oil bleachers Paper water proofers Paper water proofers Pencil manufacturers Perfume manufacturers Perfume manufacturers Photoengravers Photoengravers Photographers Platinum polishers Porcelain decorators Pottery frosters Pottery glazers Pottery glazers Printers Railroad engineers Refractory-brick manufacturers Shingle manufacturers Shingle manufacturers Silk-screen manufacturers Soap manufacturers Sponge bleachers Steel workers Tanners Textile workers Wallpaper printers Wax workers Wacid presenvative workers
Furniture polishers	waiipaper printers Wax workers
Glass-fibre manufacturers	Welders
Glue manufacturers	Wood-preservative workers
Histology technicians	Wood stainers
JEWEIEIS	

^aIARC 1990

duration of exposure; the survey only estimates the number of workers potentially exposed to chemicals in the workplace.

In a survey of workers in pigment factories in England that produced strontium and lead chromate, the concentrations of chromium in the whole blood in exposed workers ranged from 3 to 216 μ g/L, compared to a level of <1 μ g/L for the nonoccupationally exposed population (McAughey et al. 1988). The corresponding concentrations in the urine of exposed workers and the unexposed population were 1.8–575 μ g chromium/g creatinine and <0.5 μ g chromium/g creatinine, respectively (McAughey et al. 1988). Other investigators have found a higher lung burden for chromium in occupational groups than in unexposed groups. The median concentration of chromium in the lungs of deceased smelter workers in Sweden was 450 μ g/kg (wet weight), compared to a value of 110 μ g/kg (wet weight) for rural controls and 199 μ g/kg (wet weight) for urban controls (Gerhardsson et al. 1988).

5.6 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 2.7, 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 living in vicinities where there are chromium waste sites nearby may be exposed to chromium to a greater extent than adults through inhalation of chromium particulates and through contact with contaminated soils. One study has shown that the average concentration of chromium in the urine of children at ages five and younger was significantly higher than in adults residing near sites where chromium waste slag was used as fill material (Fagliano et al. 1997). The tendency of young children to ingest soil, either intentionally through pica or unintentionally through hand-to-mouth activity, is well documented. These behavioral traits can result in ingestion of chromium present in soil and dust. Soil

5. POTENTIAL FOR HUMAN EXPOSURE

may affect the bioavailability of contaminants in several ways. The most likely manner is by acting as a competitive sink for the contaminants. In the presence of soil, the contaminants will partition between absorption by the gut and sorption onto the soil particles. If a soil has a longer residence time in the gut than food particles, sorption may enhance the overall absorption of the contaminant (Sheppard et al. 1995). If the contaminant is irreversibly bound to soil particles, the contaminant is unlikely to be absorbed in the gastrointestinal tract. Hexavalent chromium exists in soils as a relatively soluble anion and may be present in bioavailable form. In contrast, chromium(III) present in soil is generally not very soluble or mobile under most environmental conditions and is not readily bioavailable (James et al. 1997). Studies discussing the oral absorption of chromium in rats from a soil surface in which 30% of the chromium was in hexavalent form and 70% was in trivalent form suggested that while absorption in animals is quite low, chromium appeared to be better absorbed from soil than from soluble chromate salts (Witmer et al. 1989, 1991). However, less than half of the administered dose of chromium could be accounted for in this study, and in separate experiments with low dosages administered to the rats, the control animals actually had higher concentrations of chromium than the animals that were administered the oral dose. Children may accidently ingest chromium picolinate in households whose members use this product as a dietary supplement unless it is well stored and kept away from children. Small amounts of chromium are used in certain consumer products such as toners in copying machines and printers, but childhood exposure from these sources are expected to be low. Children may also be exposed to chromium from parents' clothing or items removed from the workplace if the parents are employed in a setting where occupational exposure is significant (see Section 5.5). Chromium has been detected in breast milk at concentrations of $0.06-1.56 \mu g/L$ (Casey and Hambidge 1984), suggesting that children could be exposed to chromium from breast-feeding mothers. Studies on mice have shown that chromium crosses the placenta and can concentrate in fetal tissue (Danielsson et al. 1982; Saxena et al. 1990a).

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to individuals who are occupationally exposed to chromium (see Section 5.5), there are several groups within the general population that have potentially high exposures (higher than background levels) to chromium. These populations include individuals living in proximity to sites where chromium was produced or sites where chromium was disposed, and individuals living near one of the NPL hazardous waste sites where chromium has been detected in some environmental media (HazDat 2000). Persons using chromium picolinate as a dietary supplement will also be exposed to higher levels of chromium than those not ingesting this product (Anderson 1998b). Like many other products used to promote weight loss or speed metabolism there is also the potential for overuse of this

product by some members of the population in order to achieve more dramatic results (Wasser et al. 1997). People may also be exposed to higher levels of chromium if they use tobacco products, since tobacco contains chromium (IARC 1980).

Workers in industries that use chromium are one segment of the population that is especially at high risk to chromium exposure. Occupational exposure from chromate production, stainless steel welding, chromium plating, and ferrochrome and chrome pigment production is especially significant since the exposure from these industries is to chromium(VI). Occupational exposure to chromium(III) compounds may not be as great a concern as exposure to chromium(VI) compounds. Among the general population, residents living near chromate production sites may be exposed to higher levels of chromium(VI) in air. Ambient concentrations as high as $2.5 \,\mu g/m^3$ chromium in air were detected in a 1977 sample from Baltimore, Maryland (EPA 1984a). People who live near chromium waste disposal sites and chromium manufacturing and processing plants may be exposed to elevated levels of chromium. The airborne concentrations of chromium(VI) and total chromium in a contaminated site in Hudson County, New Jersey, were studied (Falerios et al. 1992). The mean concentrations of both chromium(VI) and total chromium in indoor air of the contaminated site were about three times higher than the mean indoor air concentrations of uncontaminated residential sites in Hudson County. Although the mean concentration of chromium(VI) in outdoor air was much lower than the current occupational exposure limit of $50 \,\mu\text{g/m}^3$, its levels in 10 of 21 samples at the contaminated site exceeded the background urban outdoor chromium(VI) concentration of 4 ng/m³. Similarly, the total chromium concentration in 11 of 21 outdoor air samples from the contaminated site exceeded the outdoor mean concentration of 15 ng/m^3 for urban New Jersey. However, recent sampling data from Hudson County, NJ have shown that more than two-thirds of previously sampled sites contaminated with chromite ore processing residue did not have statistically significant mean concentrations greater than the background levels (Scott et al. 1997a). This data, as well as the results of a soil dispersion model (Scott et al. 1997b) suggest that heavy vehicular traffic over unpaved soil surfaces containing chromium(VI) are required for high levels of atmospheric chromium(VI) at these sites. Persons using contaminated water for showering and bathing activities may also be exposed via inhalation to potentially high levels of chromium(VI) in airborne aerosols (Finley et al. 1996a). In a field study to simulate daily bathing activity, airborne chromium(VI) concentrations were about 2 orders of magnitude greater than ambient outdoor air concentrations when water concentrations of 5.4 and 11.5 mg/L were used in the shower.

A study was conducted from September to November 1989 to determine the levels of chromium in urine and red blood cells of state employees who worked at a park (with only indirect exposure potential)

5. POTENTIAL FOR HUMAN EXPOSURE

adjacent to chromium-contaminated sites in Hudson County, New Jersey (Bukowski et al. 1991). The chromium levels in red blood cells and urine of 17 of these employees showed no differences compared to 36 employees who worked at state parks outside Hudson County. The authors concluded that urinary and blood levels of chromium are poor biological markers in gauging low-level environmental exposure to chromium. This study also concluded that chromium levels in blood and urine depended on other confounding variables, such as exercise, past employment in a chromium-exposed occupation, beer drinking, and diabetic status. Other lifestyle (e.g., smoking), dietary, or demographic factors had no measurable effect on blood and urinary chromium. These conclusions are consistent with the results of a recent study that measured the urinary excretion of chromium following oral ingestion of chromite ore processing residue material for three days (Finley and Paustenbach 1997). These results indicate no statistical difference in mean urinary chromium concentrations in groups of individuals exposed to chromite ore processing residue material versus the control group. High levels of chromium were detected in the urine and hair of individuals living near a chromite ore-processing plant in Mexico (Rosas et al. 1989), and does suggest the possibility of using these media as biological markers in gauging long term high-level environmental exposure to chromium.

Elevated levels of chromium in blood, serum, urine, and other tissues and organs have been observed in patients with cobalt-chromium knee and hip arthroplasts (Coleman et al. 1973; Michel et al. 1987; Sunderman et al. 1989).

The chromium content in cigarette tobacco from the United States has been reported to be 0.24–6.3 mg/kg (IARC 1980), but neither the chemical form nor the amount of chromium in tobacco smoke is known. People who use tobacco products may be exposed to higher than normal levels of chromium.

5.8 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 chromium 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 chromium.

5. POTENTIAL FOR HUMAN EXPOSURE

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.

5.8.1 Identification of Data Needs

Physical and Chemical Properties. As seen in Section 3.2, the relevant physical and chemical properties of chromium and its compounds are known (Hartford 1979; Weast 1985) and prediction of environmental fate and transport of chromium in environmental media is possible. However, the physical or chemical forms and the mode by which chromium(III) compounds are incorporated into biological systems are not well characterized. The determination of the solubilities of hexavalent chromium compounds in relevant body fluids (e.g., the solubility of chromates in lung fluid) may also be helpful.

Production, Import/Export, Use, Release, and Disposal. Knowledge of a chemical's production volume is important because it may indicate environmental contamination and human exposure. If a chemical's production volume is high, there is an increased probability of general population exposure via consumer products and environmental sources, such as air, drinking water, and food. Data concerning the production (Hartford 1979; SRI 1997), import (NTDB 1998), and use (CMR 1988; EPA 1984a; IARC 1990; USDI 1988a) of commercially significant chromium compounds are available. It does not appear that chromium is used to process foods for human consumption or is added to foods other than diet supplements. Consumer exposure to chromium occurs mostly from natural food (Bennett 1986; EPA 1984a; Kumpulainen et al. 1979), but this exposure will increase particularly for people who consume acidic food cooked in stainless steel utensils (Anderson 1981; EPA 1984a). Exposure to chromium occurs to a much lesser extent from products such as toners of photocopying machines, some wood treatment chemicals, and through other chromium-containing consumer products (CMR 1988; EPA 1984a; IARC 1990; USDI 1988a).

The TRI97 (1999), which became available in 1999, has been used in this profile. As can be seen in Table 5-2, the largest amount of chromium from production and user facilities is disposed of on land or transferred to an off-site location. More detailed site-and medium-specific (e.g., air, water, or soil) release data for chromium that is disposed of off-site are necessary to assess the exposure potential to these compounds from different environmental media and sources. There are EPA guidelines regarding the

disposal of chromium wastes and OSHA regulations regarding the levels of chromium in workplaces (EPA 1988a; OSHA 1998a).

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1997, became available in 1999. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. Information is available to permit assessment of the environmental fate and transport of chromium in air (Schroeder et al. 1987; Scott et al. 1997a, 1997b), water (Carey 1982; EPA 1980, 1984a; Fishbein 1981; Schmidt and Andren 1984) and soil (Bartlett 1991; Calder 1988; Cary 1982). Chromium is primarily removed from the atmosphere by fallout and precipitation. By analogy with copper, the residence time of chromium in the atmosphere is expected to be <10 days (Nriagu 1979). Most of the chromium in lakes and rivers will ultimately be deposited in the sediments. Chromium in the aquatic phase occurs in the soluble state or as suspended solids adsorbed onto clayish materials, organics, or iron oxides (Cary 1982). Most of the soluble chromium is present as chromium(VI) or as soluble chromium(III) complexes and generally accounts for a small percentage of the total (Cary 1982). Additional data, particularly regarding chromium's nature of speciation, would be necessary to fully assess chromium's fate in air. For example, if chromium(III) oxide forms some soluble salt in the air due to speciation, its removal by wet deposition will be faster. No data regarding the half-life of chromium in the atmosphere or a measure of its persistence are available. In aquatic media, sediment will be the ultimate sink for chromium, although soluble chromates may persist in water for years (Cary 1982; EPA 1984a). Additional data elucidating the nature of speciation of chromium in water and soil would also be desirable.

Bioavailability from Environmental Media. The bioavailability of chromium compounds from contaminated air, water, soil, or plant material in the environment has not been adequately studied. Absorption studies of chromium in humans and animals provide information regarding the extent and rate of inhalation (Cavalleri and Minoia 1985; Kiilunen et al. 1983; Langård et al. 1978), and oral exposure (Anderson 1981, 1986; Anderson et al. 1983; Donaldson and Barreras 1966; Randall and Gibson 1987; Suzuki et al. 1984). These studies indicate that chromium(VI) compounds are generally more readily absorbed from all routes of exposure than are chromium(III) compounds. This is consistent, in part, with the water solubilities of these compounds (Bragt and van Dura 1983). The bioavailability of both forms

5. POTENTIAL FOR HUMAN EXPOSURE

is greater from inhalation exposure than from ingestion or dermal exposure. The bioavailability of chromium from soil depends upon several factors (Witmer et al. 1989). Factors that may increase the mobility of chromium in soils include the speculated conversion of chromium(III) to chromium(VI), increases in pH, and the complexation of chromium(III) with organic matter from water-soluble complexes. Data on the bioavailability of chromium compounds from actual environmental media and the difference in bioavailability for different media need further development.

Food Chain Bioaccumulation. Chromium does not bioconcentrate in fish (EPA 1980, 1984a; Fishbein 1981; Schmidt and Andren 1984). There is no indication of biomagnification of chromium along the aquatic food chain (Cary 1982). Some data indicate that chromium has a low mobility for translocation from roots to above-ground parts of plants (Cary 1982; WHO 1988). However, more data regarding the transfer ratio of chromium from soil to plants and biomagnification in terrestrial food chains would be desirable.

Exposure Levels in Environmental Media. The atmospheric total chromium concentration in the United States is typically <10 ng/m³ in rural areas and 10–30 ng/m³ in urban areas (Fishbein 1984). The chromium concentrations in U.S. drinking water typically range from 0.4 to 8.0 μ g/L, with a mean value of 1.8 μ g/L (Greathouse and Craun 1978). The chromium level in soils varies greatly and depends on the composition of the parent rock from which the soils were formed. Basalt and serpentine soils, ultramafic rocks, and phosphorites may contain chromium as high as a few thousand mg/kg (Merian 1984), whereas soils derived from granite or sandstone will have lower concentrations of chromium (Swaine and Mitchell 1960). The concentration range of chromium in 1,319 samples of soils and other surficial materials collected in the conterminous United States was 1–2,000 mg/kg, with a geometric mean of 37 mg/kg (USGS 1984). There is a large variation in the available data regarding the levels of chromium in foods (EPA 1984a). Concentrations ranges are 30–230 μ g/kg in wegetables, 20–510 μ g/kg in fruits, 40–220 μ g/kg in grains and cereals, and 110–230 μ g/kg in meats and fish (EPA 1984a). It would be useful to develop nationwide monitoring data on the levels of chromium in U.S. ambient air and drinking water, and these data should quantitate levels of both chromium(III) and chromium(VI) and not just total chromium.

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

313

Exposure Levels in Humans. The general population is exposed to chromium by inhaling ambient air and ingesting food and drinking water containing chromium. Dermal exposure of the general public to chromium can occur from skin contact with certain consumer products that contain chromium or from contact with chromium contaminated soils. Some of the consumer products known to contain chromium are certain wood preservatives, cement, cleaning materials, textiles, and leather tanned with chromium (WHO 1988). However, no quantitative data for dermal exposure to chromium-containing consumer products were located. Levels of chromium in ambient air ($<0.01-0.03 \mu g/m^3$) (Fishbein 1984) and tap water (<2 μ g/L) (Greathouse and Craun 1979) have been used to estimate the daily intake of chromium via inhalation ($<0.2-0.6 \mu g$) and via tap water ($<4 \mu g$). These estimates are based on an air inhalation rate of 20 m^3 /day and a drinking water consumption rate of 2 L/day. The daily chromium intake for the U.S. population from consumption of selected diets (diets with 25 and 43% fat) has been estimated to range from 25 to 224 µg, with an average of 76 µg (Kumpulainen et al. 1979). The average value is close to a value of 60 µg reported by Bennett (1986). However, few data on the levels of chromium in body tissues or fluids for populations living near hazardous waste sites are available. Such data could be a useful tool as an early warning system against harmful exposures. In addition, there is a need for data on the background levels of chromium in body fluids of children. Such data would be important in assessing the exposure levels of this group of people.

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

Exposures of Children. Limited data exist regarding exposure and body burdens of chromium in children. Chromium has been detected in breast milk at concentrations of 0.06–1.56 µg/L (Casey and Hambidge 1984), suggesting that children could be exposed to chromium from breast-feeding mothers. Studies in mice have shown that chromium crosses the placenta and can concentrate in fetal tissue (Danielsson et al. 1982; Saxena et al. 1990a). Because children living near areas contaminated with chromium have been shown to have elevated chromium levels in urine as compared to adults (Fagliano et al. 1997), additional body burden studies are required to evaluate the exposures and the potential consequences this might have upon children. This is particularly important around heavily contaminated soils where children may be exposed dermally or through inhalation of soil particulates during play activities. These studies may determine if children may be more susceptible than adults to the toxic effects of chromium including immunosensitivity. Studies are necessary that examine children's weight-adjusted intake of chromium and determine how it compares to that of adults. Since chromium is often detected in soil surfaces and children ingest soil either intentionally through pica or unintentionally through hand-to-mouth activity, pica is a unique exposure pathway for children. Studies have shown that

although absorption of chromium is low, it may be enhanced slightly from contaminated soil surfaces (Witmer et al. 1989, 1991).

Child health data needs relating to susceptibility are discussed in 2.12.2 Identification of Data Needs: Children's Susceptibility.

Exposure Registries. Chromium is currently one of the chemicals for which a subregistry has been established in the National Exposure Registry. 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 chromium.

5.8.2 Ongoing Studies

The database of federal research programs in progress (FEDRIP) indicates several current projects that may fill some existing data gaps. Dr. Syed M. Naqvi at Southern University is investigating the extent to which chromium can bioaccumulate in crayfish tissues consumed by humans (FEDRIP 1999).

Dr. Gordon E. Brown, Jr. at Stanford University is examining the possibility of using the results of spectroscopic measurements in developing a predictive macroscopic model of sorption behavior and fluid-solid partitioning of chromium (FEDRIP 1999). Dr. Kathleen Dixon at the University of Cincinnati is investigating the role of the biotransformation of chromium within the cell in the mutagenic activation of the compound (FEDRIP 1999). Dr. Harold F. Hemond at the Massachusetts Institute of Technology is investigating the quantification of episodic and chronic releases of chromium from sediments into the Aberjona watershed (FEDRIP 1999). Dr. Andrew J. Friedland at Dartmouth College is attempting to establish the mobility rates of metals such as chromium in terrestrial ecosystems (FEDRIP 1999). Dr. Friedland is using over 100 years of atmospheric deposition records and is evaluating potential release rates of metals into surface water, aquatic ecosystems, and groundwater.

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