6. POTENTIAL FOR HUMAN EXPOSURE

6.1   OVERVIEW

Zinc has been identified in at least 985 of the 1,662 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2005). However, the number of sites evaluated for zinc is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, 969 are located within the United States, and 2, 12, and 2 sites are located in the Commonwealth of Guam, Puerto Rico, and the Virgin Islands, respectively.
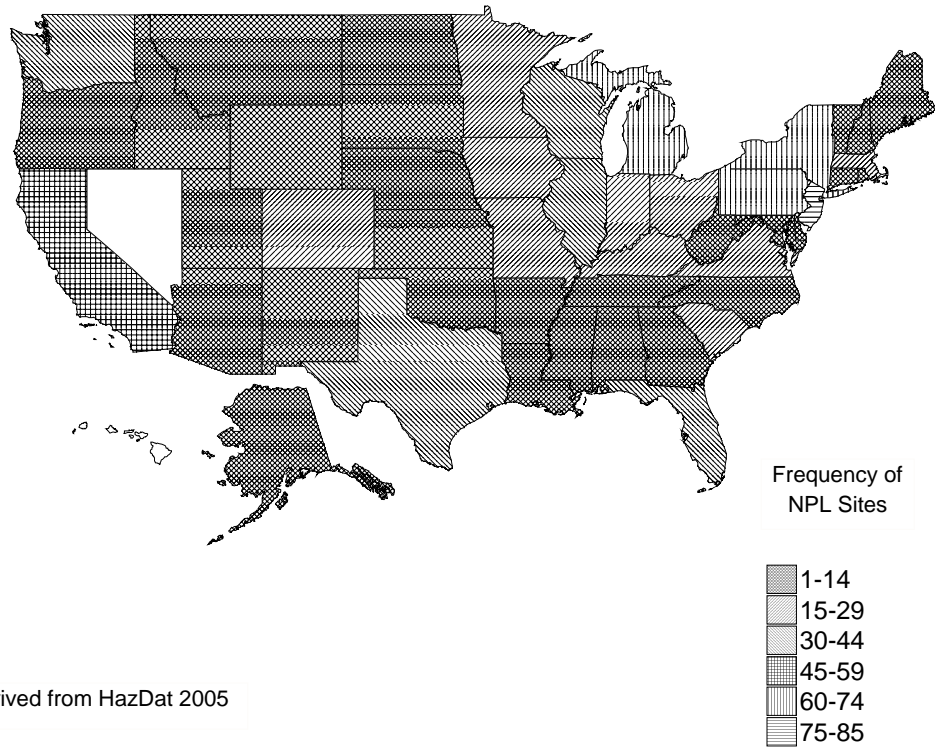
Zinc is an element commonly found in the Earth's crust. It is released to the environment from both natural and anthropogenic sources; however, releases from anthropogenic sources are greater than those from natural sources. The primary anthropogenic sources of zinc in the environment (air, water, soil) are related to mining and metallurgic operations involving zinc and use of commercial products containing zinc. Worldwide, releases to soil are probably the greatest source of zinc in the environment. The most important sources of anthropogenic zinc in soil come from discharges of smelter slags and wastes, mine tailings, coal and bottom fly ash, and the use of commercial products such as fertilizers and wood preservatives that contain zinc. Zinc does not volatilize from soil. Although zinc usually remains adsorbed to soil, leaching has been reported at waste disposal sites. Zinc does not volatilize from water but is deposited primarily in sediments through adsorption and precipitation. Severe zinc contamination tends to be confined to areas near emission sources. Large amounts of contaminated soil would need to be ingested in order to reach the registered dietary index value of 3.3–3.8 mg of zinc a day. It is therefore unlikely that the zinc found in the contaminated soil would pose a health risk if ingested.

Zinc is capable of forming complexes with a variety of organic and inorganic groups (ligands). Biological activity can affect the mobility of zinc in the aquatic environment, although the biota contains relatively little zinc compared to the sediments. Zinc bioconcentrates moderately in aquatic organisms; bioconcentration is higher in crustaceans and bivalve species than in fish. Zinc does not concentrate in plants, and it does not biomagnify through terrestrial food chains.

In some fish, it has been observed that the level of zinc found in their bodies did not directly relate to the exposure concentrations. A recent study shows that bioaccumulation of zinc in fish is inversely related to

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

Frequency of
NPL Sites

1-14
15-29
30-44
45-59
60-74
75-85

Derived from HazDat 2005

the aqueous exposure (McGeer et al. 2003). This evidence suggests that fish placed in environments with lower zinc concentrations can sequester zinc in their bodies.

There are few data regarding the speciation of zinc released to the atmosphere. Zinc is removed from the air by dry and wet deposition, but zinc particles with small diameters and low densities suspended in the atmosphere travel long distances from emission sources.

Zinc has been detected in air, surface water, groundwater, and soil; the frequency of detection and the concentrations are greatest near source areas (e.g., hazardous waste sites and industrial areas such as lead smelters). In a survey by the National Air Surveillance Network, the mean concentration of zinc in the air in the United States in 1977–1979 was 0.02–0.16 $\mu g/m^3$ for urban air compared to 0.01–0.05 $\mu g/m^3$ for rural air. The concentrations of zinc in the air of remote areas range from <0.003 to 0.027 $\mu g/m^3$. The mean concentrations of zinc in ambient water and drinking water range from 0.02 to 0.05 mg/L and from 0.01 to 0.1 mg/L, respectively. The concentration of zinc in drinking water can often be higher than the concentration in the raw water from which the drinking water was obtained because zinc may leach from transmission and distribution pipes. The concentration of zinc in standing water from galvanized household water pipes was ≤1.3 mg/L (Sharrett et al. 1982a). The concentration of zinc in cultivated soils in the United States ranged from <5 to 400 mg/kg, with a mean of 36 mg/kg, compared to a range of <10–2,000 mg/kg, with a mean of 51 mg/kg, in uncultivated soils; this probably results from the differences in soils used for farming rather than the use of zinc in agriculture. Concentrations of zinc can be high in soils from contaminated sites, such as waste dumps.

The concentrations of zinc in various foods and human tissues have also been determined. Certain population groups may be exposed to higher concentrations of zinc than the general population. People who work in coal mines, people who work with the refining and smelting of nonferrous metals, and people who live near waste sites and metal smelting operations may be exposed to high levels of zinc. A study of the tissue of deceased copper smelter workers in Sweden showed that they had, on average, 58.9 and 31.5 mg/kg wet weight of zinc in the liver and kidney, respectively, as compared to the controls, who had 47.2 and 23.3 mg/kg wet weight of zinc in the liver and kidney, respectively. The controls, however, had a higher concentration of zinc in the hair (233 mg/kg as opposed to the smelter workers who had 212 mg/kg) (Gerhardsson et al. 2002). People who consume large amounts of foods high in zinc content, such as oysters and mussels, may also be exposed to elevated levels of zinc. The zinc body burdens of the copper smelter workers were not significantly different than that of the controls. Higher exposure may or may not be manifested as increased body burden in the exposed individuals.

According to NHANES 1999–2000 dietary data, a large portion of obese people over the age of 50 are not getting the recommended amount of zinc (Bermudez et al. 2003). The RDA for zinc is 11 mg/day for men and 8 mg/day for women (see Section 3.1). Much of the human zinc intake comes from eating meat and meat products. A typical Italian diet contains about10.6 mg of dietary zinc per day, where 4.3 mg of zinc comes from meat and meat products (Lombardi-Boccia et al. 2003). Nonvegetarians absorb a higher percentage of zinc (3.7 mg/day) than vegetarians (2.4 mg/day) (Hunt 2003; Hunt et al. 1998). Infants also need zinc, and the RDA for zinc in pregnant and nursing mothers is 12 mg/day. A recent study of breast milk in lactating mothers showed an average zinc concentration of about 5.65 mg/L. This average did not vary much depending on the age of the mother (Honda et al. 2003).

6.2   RELEASES TO THE ENVIRONMENT

The TRI data should be used with caution because only certain types of facilities are required to report (EPA 1997). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the Toxics Release Inventory only if they employ 10 or more full-time employees; if their facility is classified under Standard Industrial Classification (SIC) codes 20–39; and if their facility produces, imports, or processes ≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 1997).

Zinc is commonly found in the earth's crust, and natural releases to the environment can be significant. In addition, zinc is one of the most widely used metals in the world. The major industrial sources of zinc include electroplating, smelting and ore processing, and drainage from both active and inactive mining operations (Mirenda 1986). Furthermore, zinc is an important component of brass, bronze, die casting metal, other alloys, rubber, and paints. The environmental releases of zinc from sources of human origin far exceed the releases from natural sources (Fishbein 1981).

6.2.1   Air

Estimated releases of 0.91 million pounds (~413 metric tons) of zinc to the atmosphere from 389 domestic manufacturing and processing facilities in 2002, accounted for about 1.9% of the estimated total environmental releases from facilities required to report to the TRI (TRI02 2004). These releases are summarized in Table 6-1.

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Zinc[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
AL	9	25,166	26,199	0	98,857	18,716	51,365	117,573	168,938
AR	8	12,295	5	0	141,993	7,440	154,293	7,440	161,733
AZ	2	500	0	0	0	0	500	0	500
CA	21	4,853	19,219	0	1,155,909	339	1,161,251	19,069	1,180,320
CO	5	1,385	383	0	13,847	5,808	12,978	8,445	21,423
CT	3	500	0	0	0	0	500	0	500
DE	1	No data	No data	No data	No data	No data	No data	No data	No data
FL	5	1,277	5	0	0	3,800	1,282	3,800	5,082
GA	9	521	0	0	28,010	420	521	28,430	28,951
IA	11	15,806	82	0	48,666	0	15,887	48,666	64,553
ID	3	6,863	0	0	21,957,330	520	21,964,193	520	21,964,713
IL	24	134,748	750	0	680,474	30,373	134,748	711,597	846,345
IN	20	12,445	267	0	44,651	40,370	36,473	61,261	97,734
KS	4	4,541	0	0	36,921	4	4,541	36,925	41,466
KY	15	16,266	0	0	35,572	618	17,866	34,590	52,456
LA	13	12,382	0	0	54,683	0	12,382	54,683	67,065
MA	6	270	178	0	0	468	270	646	916
MD	3	122	0	0	5,537	0	122	5,537	5,659
ME	1	0	0	0	5,569	1,646	0	7,215	7,215
MI	15	4,927	9	0	660,702	10,912	114,609	561,941	676,550
MN	4	249	0	0	0	0	249	0	249
MO	9	5,391	0	0	77,964	0	73,772	9,583	83,355
MS	6	720	251	0	9,025	0	9,746	250	9,996
NC	19	1,203	0	0	342,077	2,487,306	1,203	2,829,383	2,830,586
NE	2	3,194	0	0	5	10	3,199	10	3,209
NH	1	950	0	0	0	5	950	5	955
NJ	7	10,681	0	0	5,700	14,623	10,681	20,323	31,004
NM	1	0	0	0	252,500	0	252,500	0	252,500
NV	2	972	0	0	70,226	0	71,198	0	71,198
NY	10	8,103	0	0	11,278	525	18,203	1,703	19,906
OH	32	85,004	6,334	0	9,415,075	6,165,482	9,389,168	6,282,727	15,671,896
OK	8	17,406	50	0	0	42,403	17,456	42,403	59,859

Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Zinc[a]

							Reported amounts released in pounds per year[b]		
								Total release	
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
OR	1	0	0	0	37,960	0	37,960	0	37,960
PA	20	64,389	144	0	353,840	58,168	64,709	411,832	476,541
PR	2	0	0	0	0	5	0	5	5
RI	3	930	0	0	0	5	930	5	935
SC	8	27,976	168	0	20,724	7,596	35,372	21,092	56,464
SD	2	1,085	0	0	3,218	0	1,335	2,968	4,303
TN	12	9,000	705	0	164,297	22,208	23,431	172,779	196,210
TX	19	46,875	2,211	0	63,988	121,879	73,195	161,758	234,953
UT	4	119	0	0	8,009	8	6,613	1,523	8,136
VA	9	340,253	1,316	0	38,919	2,986	369,093	14,381	383,474
WA	1	No data	No data	No data	No data	No data	No data	No data	No data
WI	17	4,738	250	0	1,228,914	4,607	4,988	1,233,521	1,238,509
WV	9	26,652	0	0	52,674	6,111	79,326	6,111	85,437
WY	3	208	0	0	42,767	0	39,672	3,303	42,975
Total	389	910,964	58,525	0	37,167,881	9,055,361	34,268,728	12,924,002	47,192,731

Source: TRI02 2004 (Data are from 2002)

[a]The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b]Data in TRI are maximum amounts released by each facility.
[c]Post office state abbreviations are used.
[d]Number of reporting facilities.
[e]The sum of fugitive and point source releases are included in releases to air by a given facility.
[f]Surface water discharges, wastewater treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g]Class I wells, Class II-V wells, and underground injection.
[h]Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other on-site landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i]Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown
[j]The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k]Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Natural emissions of zinc and its compounds to air are mainly due to windborne soil particles, volcanic emissions, and forest fires. The global flux of zinc due to erosion is estimated to be 915,000 tonnes/year; of this total, 681,000 tonnes comes from high-temperature thermal vents in mid-ocean ridges (WHO 2001). Volcanic release of zinc has been estimated to be around 35,800 tonnes/year (Lantzy 1979). The eruption of Mt. Pinatubo alone released an estimated 800,000 tonnes of zinc into the atmosphere in 1991 (Garrett 2000). Other natural sources of zinc in air are biogenic emissions and sea salt sprays with annual amounts estimated to be 8,100 and 440 metric tons, respectively (Nriagu 1989).

Anthropogenic releases of zinc and its compounds to the atmosphere are from dust and fumes from mining, zinc production facilities, processing of zinc-bearing raw materials (e.g., lead smelters), brass works, coal and fuel combustion, refuse incineration, and iron and steel production (EPA 1980d; Ragaini et al. 1977). In urban East St. Louis, Illinois, industrial complexes, such as smelters, accounted for about 86% of fine and course particulate matter emitted into air. In southeastern Chicago, Illinois, incinerator emissions accounted for 86% of fine particulate in the atmosphere while urban dust account for 93% of the course particulate emissions (Sweet et al. 1993). Estimated atmospheric zinc loss is 100 g/ton of zinc mined, and most of the loss comes from handling raw and concentrated ore and wind erosion of tailing piles (Lloyd and Showak 1984). Average zinc emissions to the atmosphere from stationary sources in the United States were 151,000 tons/year (137,000 metric tons/year) for 1969–1971 (Fishbein 1981). Based on emission studies in Western Europe, the United States, Canada, and the former Soviet Union, total worldwide zinc emissions to air were calculated to range from 70,250 to 193,500 metric tons in 1983. Emissions from the nonferrous metal industry account for the largest fraction of zinc emitted (50–70%) (Nriagu and Pacyna 1988). However, emissions have decreased considerably since the 1970s and 1980s as a result of improvements in contemporary zinc production facilities. Zinc emissions decreased 73% for air and 83% for water during the years 1985–1995 (WHO 2001).

According to the TRI, estimated totals of 910,964 pounds (413 metric tons) of zinc (dust and fume) and 6,415,067 pounds (2,909 metric tons) of zinc compounds, amounting to about 1.9 and 0.92%, respectively, of the total environmental on-site releases, were discharged into the atmosphere in the United States in 2001 from mining, manufacturing, processing, and electrical power generation industries listed in Tables 6-1 and 6-2 (TRI02 2004). Data for stack/point source emissions indicate releases of 495,206 pounds (224 metric tons) of zinc (dust and fume) and 4,617,457 pounds (2,094 metric tons) of zinc compounds, while data for fugitive source emission indicate a release of 375,586 pounds (170 metric tons) of zinc (dust and fume) and 1,542,235 pounds (700 metric tons) of zinc compounds. The TRI data

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Zinc Compounds[a]

							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
AK	5	57,736	892	10,000,000	295,817,343	0	305,875,971	0	305,875,971
AL	91	146,282	73,856	77,052	5,220,635	7,077,255	4,908,757	7,686,323	12,595,081
AR	78	81,410	102,806	6,991	696,606	2,389,162	336,042	2,940,934	3,276,976
AZ	21	32,825	20,160	144,780	25,217,086	2,004	25,376,638	40,217	25,416,855
CA	119	63,649	19,734	9,665	595,116	20,349	398,970	309,543	708,513
CO	19	57,253	344	25,996	198,087	10,270	176,373	115,577	291,950
CT	32	5,722	28,075	0	133,452	134,880	7,120	295,010	302,129
DE	13	10,020	17,921	0	107,926	17,708	58,714	94,861	153,575
FL	66	72,363	93,297	48,570	2,000,003	88,270	1,937,933	364,570	2,302,503
GA	114	244,067	98,139	0	1,233,070	210,195	1,099,676	685,796	1,785,472
HI	1	20	0	0	37,942	0	20	37,942	37,962
IA	95	77,263	117,986	31,317	1,768,665	95,611	488,463	1,602,378	2,090,841
ID	12	41,585	2,108	0	3,669,321	95	3,700,829	12,280	3,713,109
IL	221	395,491	149,295	163,316	27,247,648	1,294,295	22,947,032	6,303,014	29,250,046
IN	157	723,924	286,946	15,177	37,744,073	24,151,185	8,875,522	54,045,784	62,921,306
KS	42	97,372	1,625	1,685	450,609	101,544	304,823	348,012	652,835
KY	92	83,843	125,476	4,375	2,453,652	183,585	2,167,004	683,927	2,850,931
LA	77	147,835	81,079	167,914	4,761,318	340,895	3,238,709	2,260,332	5,499,041
MA	50	9,766	2,381	0	363,863	136,582	35,580	477,012	512,592
MD	34	17,599	23,384	10,389	205,405	149,224	178,885	227,116	406,001
ME	8	16,887	16,090	0	449,015	5,450	174,943	312,499	487,442
MI	159	213,987	286,754	16,000	43,809,978	423,988	909,641	43,841,066	44,750,707
MN	55	19,108	49,405	0	1,393,144	329,519	507,238	1,283,938	1,791,176
MO	97	565,546	27,386	20,266	31,884,266	142,655	32,046,061	594,058	32,640,118
MS	54	256,284	98,069	375,083	311,418	174,217	709,670	505,401	1,215,070
MT	6	6,244	21	0	10,787,188	1,745	10,775,448	19,750	10,795,198
NC	99	45,630	24,744	39,813	1,600,363	305,408	827,882	1,188,075	2,015,958
ND	4	760	23	0	180,026	0	77,783	103,026	180,809
NE	42	237,066	6,864	0	635,674	3,396,549	566,918	3,709,235	4,276,152
NH	10	333	825	0	5,165	5,467	2,148	9,642	11,791
NJ	80	20,689	64,099	6,287	512,445	1,109,971	131,391	1,582,100	1,713,491
NM	11	2,660	670	0	515,365	0	367,346	151,349	518,695
NV	21	6,904	1,006	0	13,889,325	26,367	13,893,110	30,492	13,923,602
NY	76	86,776	64,436	0	1,089,648	113,112	495,131	858,840	1,353,971
OH	298	216,289	305,502	480,784	13,434,185	1,583,235	2,138,108	13,881,887	16,019,995

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Zinc Compounds[a]

| | | | | | | | Reported amounts released in pounds per year[b] | | |
| | | | | | | | Total release | | |
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
OK	50	24,320	14,242	88,407	1,035,166	665,664	489,512	1,338,287	1,827,799
OR	31	17,533	19,513	0	262,676	267,398	54,083	513,037	567,120
PA	187	1,452,852	198,276	73,781	11,446,276	22,981,774	2,213,480	33,939,479	36,152,959
PR	15	3,800	463	0	31,944	272,783	35,858	273,133	308,991
RI	6	217	45	0	65,720	3,314	217	69,079	69,296
SC	76	213,093	47,512	14,331	1,823,765	13,098,684	1,644,194	13,553,191	15,197,385
SD	12	5,521	59	5	1,067,005	0	1,053,460	19,130	1,072,590
TN	118	229,905	90,647	12,856	24,051,495	479,494	22,909,614	1,954,784	24,864,397
TX	211	201,120	344,154	2,103,302	2,913,177	344,478	2,118,673	3,787,557	5,906,230
UT	24	12,446	3,747	0	6,728,264	270,481	6,738,249	276,689	7,014,938
VA	62	95,445	70,786	3,429	4,932,625	679,941	848,684	4,933,543	5,782,227
VT	3	0	0	0	46,117	0	0	46,117	46,117
WA	25	15,956	12,218	0	299,308	27,754	120,295	234,941	355,236
WI	108	62,409	17,693	4,857	3,218,796	168,323	110,208	3,361,870	3,472,078
WV	34	14,267	95,866	0	1,323,140	192,671	1,132,148	493,795	1,625,944
WY	7	4,993	2,410	0	140,640	9,543	119,725	37,861	157,586
Total	3,328	6,415,067	3,109,033	13,946,427	589,805,136	83,483,093	485,324,282	211,434,474	696,758,756

Source: TRI02 2004 (Data are from 2002)

[a]The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b]Data in TRI are maximum amounts released by each facility.
[c]Post office state abbreviations are used.
[d]Number of reporting facilities.
[e]The sum of fugitive and point source releases are included in releases to air by a given facility.
[f]Surface water discharges, wastewater treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g]Class I wells, Class II-V wells, and underground injection.
[h]Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other on-site landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i]Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown
[j]The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k]Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

should be used with caution since only certain facilities are required to report. This is not an exhaustive list.

Zinc has been identified in air at 37 sites collected from the 985 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2005).

6.2.2   Water

Estimated releases of 0.059 million pounds of zinc to surface water from 389 domestic manufacturing and processing facilities in 2002, accounted for about 0.1% of the estimated total environmental releases (TRI02 2004). This value includes the amount that was released to publicly owned treatment works (POTWs) (TRI02 2004). These releases are summarized in Table 6-1.

Zinc and its compounds are found in the earth's crust and are present in most rocks, certain minerals, and some carbonate sediments. As a result of weathering of these materials, soluble compounds of zinc are formed and may be released to water (NAS 1977). The largest input of zinc to water results from erosion of soil particles containing natural traces of zinc (45,400 metric tons/year) (EPA 1980d). Erosion resulting from human activities accounts for 70% of this soil loss; geologic or natural erosion constitutes the other 30% (EPA 1980d). However, this source of low levels of zinc is widely dispersed and is, therefore, unlikely to elevate aquatic concentrations significantly. Zinc flux to the oceans from high temperature hydrothermal fluids in mid-ocean ridges has been estimated to be approximately 681,000 metric tons/year (WHO 2001).

Urban runoff, mine drainage, and municipal and industrial effluents are smaller but more concentrated sources of zinc in water. Davis et al. (2001) estimated the zinc loadings in urban storm water runoff. In this study, buildings and automobiles were found to contribute 95% of loadings (0.646 kg/ha/year) to storm water runoff in urban environments. Data from this study are summarized in Table 6-3. The Nationwide Urban Runoff Program (NURP), initiated to evaluate the significance of priority pollutants in urban storm water runoff, reports a frequency of detection for zinc of 95%, with a concentration range of 0.01–2.4 mg/L (Cole et al. 1984). Industries that discharge large quantities of zinc directly to water include iron and steel, zinc smelting, plastics, and electroplating (EPA 1980d). The arithmetic mean concentration of zinc in influents of 239 waste water treatment plants in the United States was 0.7 mg/L, with minimum and maximum concentrations of 0.0001 and 28.7 mg/L, respectively (Minear et al. 1981). Accidental zinc discharges to water are most often associated with smelting and refining operations. Zinc

Table 6-3. Zinc Loadings in Urban Storm Water Runoff[a]

	Rate	Unit value	Loading (kg/ha/year)	Percent of total
Buildings				
Siding	180,000 m^2/ha/year	2,100 $\mu g/m^2$		58
Roof	450,000 L/ha/year	100 μg/L		7
Total			0.423	65
Autos				
Brakes	240,000 km/ha/year	88 μg/km	0.021	3
Tires	48,000 g tire/ha/year	3,400 μg/g	0.163	25
Oil leakage	48 L-oil/ha/year	1.25×10^5 mg/L	0.006	1
Total			0.190	29
Total buildings and autos			0.613	95
Wet deposition			0.013	2
Dry deposition			0.020	3
Total			0.646	100

[a]Source: Davis et al. 2001

is present with cadmium and lead in these processes (NAS 1977). Urban runoff and drainage from inactive mines account for approximately 5,250 and 4,060 metric tons/year, respectively, of the total releases of zinc to water (EPA 1980d). Drainage from active mining areas is considerably less than from inactive areas because of the disposal methods currently employed. Hazardous waste sites, in which zinc has been improperly disposed of, are additional sources of the element.

Metals, such as zinc, also enter estuaries from many natural and manufactured sources. Three important sources of zinc input into surface water are metal manufacturing (33,000–178,000 metric tons/year), domestic waste water (21,000–58,000 metric tons/year), and atmospheric fallout (2,600–31,000 metric tons/year). On an annual worldwide basis, an estimated 77,000–375,000 metric tons of zinc are discharged into water from anthropogenic sources (Nriagu and Pacyna 1988). Publicly owned treatment works are the largest total point source for zinc discharges. Publicly owned treatment works receive zinc contributions from the water supply and distribution system corrosion, combined sewer area runoff, industrial wastes, and human excrement (EPA 1980d). Crawford et al. (1995) reported the direct inputs of zinc contamination to the Newark Bay Estuary as follows (kg/day): municipal treatment systems, 272.0; industry, 14.34; combined sewer overflows, 141.5; storm water runoff, 164.6; and tributary flow, 307. Indirect inputs were 934.7 kg/day. The flux of zinc into the Hudson River Estuary from sewage has decreased from 924 kg/day in 1974 to 285 kg/day in 1997 as a result of improvements in controlling discharges from municipal and industrial waste water treatment plants since the Clean Water Act was enacted in 1972 (Sanudo-Wilhelmy and Gill 1999).

According to the TRI, estimated totals of 58,525 pounds (26.5 metric tons) of zinc (dust and fume) and 3,109,033 pounds (1,410 metric tons) of zinc compounds, amounting to about 0.1 and 0.44%, respectively, of the total environmental on-site releases, were discharged into surface water in the United States in 2002 from mining, manufacturing, processing, and electrical power generation industries listed in Tables 6-1 and 6-2. Estimated totals of 0 pounds (0 metric tons) of zinc (dust and fume) and 13,946,427 pounds (6,325 metric tons) of zinc compounds, amounting to about 0.0 and 2% of the total environmental on-site releases, respectively, were injected underground in the United States in 2001 from mining, manufacturing, processing, and Resource Conservation and Recovery Act (RCRA)/Solvent Recovery industries listed in Tables 6-1 and 6-2 (TRI02 2004). The TRI data should be used with caution since only certain facilities are required to report. This is not an exhaustive list.

The concentration of zinc in drinking water may increase as a result of the distribution system and household plumbing (EPA 1987c). Common piping materials used in distribution systems often contain

zinc, as well as other metals and alloys. Trace metals may enter the water through corrosion products or simply by the dissolution of small amounts of metals with which the water comes in contact. Reactions with materials of the distribution system, particularly in soft low-pH waters, very often have produced concentrations of zinc in tap water much greater than those in the raw or treated waters at the plant of origin (NAS 1977). The total quantity of annual releases of zinc from these sources has not been estimated. Environmental toxicity of zinc in water is dependent upon the concentration of other minerals and the pH of the solution, which affect the ligands that associate with zinc (Heijerick et al. 2002a; Paquin et al. 2002; Santore 2002).

Zinc has been identified in surface water and groundwater at 393 and 685 sites, respectively, collected from the 985 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2005).

6.2.3   Soil

Estimated releases of 37 million pounds (16,856 metric tons) of zinc to soils from 389 domestic manufacturing and processing facilities in 2002, accounted for about 79% of the estimated total environmental releases from facilities required to report to the TRI (TRI02 2004). No material was released via underground injection (TRI02 2004). These releases are summarized in Table 6-1.

Limited information is available on total releases of zinc to soil. Zinc is often present in soils and grasses as a result of atmospheric deposition. Furthermore, approximately 22,000 tons (20,000 metric tons) of zinc is used in fertilizers each year in the United States (NAS 1977). The extent to which zinc may run off into soil, rivers, and streams has not been evaluated. Hazardous waste sites are additional sources of zinc in soil. Municipal sludges applied to cropland soils can also be an important source of trace metals, including zinc (Chang et al. 1987).

On a worldwide basis, an estimated 1,193,000–3,294,000 metric tons of zinc per year are released to soil from anthropogenic sources (Nriagu and Pacyna 1988). The four most important sources of zinc in soil were estimated to be smelter slugs and wastes, mine tailings, coal and bottom fly ash, and the discharge of commercial products such as fertilizers.

Tire debris contains significant quantities of zinc, which may contaminate soils near roads. For example, snow collected on soil near an expressway in Montréal, Québec (Canada) contained higher levels zinc

near the expressway. At 15 m from expressway, a snow pack concentration of 0.143 mg/L was measured, while at 150 m from the expressway, the concentration of zinc in snow was 0.029 mg/L (Loranger et al. 1996). Laboratory experiments indicated that a significant fraction of zinc may be released from tire rubber debris. Soil pH limits the mobilization of zinc in soil. Thus, zinc from tire debris will be less available and become immobile with soil interactions (Smolders and Degryse 2002).

Metallic zinc may yield soluble zinc compounds under acidic conditions where the zinc hydroxide-carbonate layer is attacked from pollutants such as sulfur dioxide. Metallic zinc is washed off slowly and forms a diffuse source of zinc release to soils. Other releases of zinc include the use of sacrificial anodes in soil to protect steel structures from corrosion (WHO 2001).

According to the TRI, estimated totals of 37,167,881 pounds (16,856 metric tons) of zinc (dust and fume) and 589,805,136 pounds (267,485 metric tons) of zinc compounds, amounting to about 79 and 85%, respectively, of the total environmental on-site releases, were released to land in the United States in 2001 from mining, manufacturing, processing, and electrical power generation industries (Tables 6-1 and 6-2) (TRI02 2004). Another 12,924,002 pounds (5,861 metric tons) of zinc (dust and fume) and 211,434,474 pounds (95,889 metric tons) of zinc compounds were transferred to off-site treatment, storage, and disposal facilities. The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

Zinc has been identified in soil and sediment at 522 and 370 sites, respectively, collected from the 985 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2005).

6.3   ENVIRONMENTAL FATE

Zinc occurs in the environment mainly in the +2 oxidation state (Lindsay 1979). Sorption is the dominant reaction, resulting in the enrichment of zinc in suspended and bed sediments (EPA 1979d). Zinc in aerobic waters is partitioned into sediments through sorption onto hydrous iron and manganese oxides, clay minerals, and organic material. The efficiency of these materials in removing zinc from solution varies according to their concentrations, pH, redox potential (Eh), salinity, nature and concentrations of complexing ligands, cation exchange capacity, and the concentration of zinc. Precipitation of soluble zinc compounds appears to be significant only under reducing conditions in highly polluted water. Generally, at lower pH values, zinc remains as the free ion. The free ion (Zn^{+2}) tends to be adsorbed and transported by suspended solids in unpolluted waters. In polluted waters in which the concentration of zinc is high,

removal of zinc by precipitation of the hydroxide is possible, particularly when the pH is >8 (EPA 1979d). In anaerobic environments and in the presence of sulfide ions, precipitation of zinc sulfide limits the mobility of zinc. The relative mobility of zinc in soil is determined by the same factors that affect its transport in aquatic systems (i.e., solubility of the compound, pH, and salinity) (Clement 1985).

Zinc is an essential nutrient that is present in all organisms. Although biota appears to be a minor reservoir of zinc relative to soils and sediments, microbial decomposition of biota in water can produce ligands, such as humic acids, that can affect the mobility of zinc in the aquatic environment through zinc precipitation and adsorption (EPA 1979d).

Zinc concentrations in the air are relatively low, except near industrial sources such as smelters. No estimate for the atmospheric lifetime of zinc is available at this time, but the fact that zinc is transported long distances in air indicates that its lifetime in air is at least on the order of days.

6.3.1   Transport and Partitioning

Air. In the atmosphere, zinc exists primarily in an oxidized form bound to aerosols, with the size of zinc particulates determined by the source of zinc emission (Nriagu and Davidson 1980; Sweet et al. 1993). A major proportion of zinc released from industrial processes is adsorbed on particulates that are small enough to be in the respirable range (Dorn et al. 1976). Wind-blown dust transports zinc bound to soil particulates into the atmosphere (EPA 1980d). The particulates may also contain other materials (Pacyna et al. 1989; Saltzman et al. 1985).

Zinc-bearing particles in the atmosphere are transported to soil and water by wet deposition (rain and snow) and dry deposition (gravitational settling and deposition on water and soil surfaces). Zinc particles with low dry deposition velocities (i.e., particles with small diameters and low densities) can be transported from their emission source to distant regions (Pacyna et al. 1989). The atmospheric wet deposition of zinc (and other trace metals) was examined at two Maryland Chesapeake Bay sites from June 1990 to July 1991 as part of the Chesapeake Bay Atmospheric Deposition Study (Scudlark et al. 1994). The average annual wet deposition at these two sites was 1,335 $\mu g/m^2$/year with 99% attributed to anthropogenic sources. As part of the Atmospheric Exchange over Lakes and Oceans Study (AEOLOS), dry deposition fluxes of zinc were measured over the southern basin of Lake Michigan near the urban area of Chicago and the nonurban area of South Haven, Michigan (Paode et al. 1998). In 1993, the average measured zinc fluxes were 200 $\mu g/m^2$/day in Chicago; 10 $\mu g/m^2$/day over southern Lake

Michigan; and 4 µg/m^2/day in South Haven, Michigan. Between 1993 and 1995, Shahin et al. (2000) estimated the dry deposition flux of zinc in Chicago to be 4.4×10^4 µg/m^2/year. Atmospheric deposition rates of zinc for Lakes Superior, Erie, and Ontario were reported to be 3,310, 2,180, and 5,650 µg/m^2/year, respectively (Nriagu et al. 1996). Detection of zinc in rain waters confirms the importance of wet precipitation in the removal of zinc particles from the atmosphere (Aten et al. 1983; Colin et al. 1990; Dasch and Wolff 1989; Golomb et al. 1997; Heaton et al. 1990). Golomb et al. (1997) measured the atmospheric deposition of zinc at Nahant, Massachusetts (near urban area of Boston) and at Truro, Massachusetts (on Cape Cod) for the years 1992–1993. Results indicated that wet deposition was a significant fraction of the total atmospheric deposition of zinc for Nahant (28%) and Truro (40%).

Water. In water, zinc occurs in the environment primarily in the +2 oxidation state. It dissolves in acids to form hydrated Zn^{+2} cations and in strong bases to form zincate anions, which are hydroxo complexes, e.g., $(Zn[OH]_3)^-$, $(Zn[OH]_4)^{2-}$, and $(Zn[OH]_4[H_2O]_2)^{2-}$ (O'Neil et al. 2001). In most waters, zinc exists primarily as the hydrated form of the divalent cation. However, the metal often forms complexes with a variety of organic and inorganic ligands (EPA 1979d, 1984b, 1987c).

Zinc can occur in both suspended and dissolved forms in surface water. Dissolved zinc may occur as the free (hydrated) zinc ion or as dissolved complexes and compounds with varying degrees of stability. Suspended (i.e., undissolved) zinc may be dissolved with changes in water conditions (e.g., pH, redox potential, solution speciation) or may sorb on to suspended matter. Gundersen and Steinnes (2003) reported that <10% of zinc was sorbed on particles or colloids in river water from two rivers with average pHs of 3.1 and 5.1 (rivers with mining activity near Roes, Norway), whereas 21% of zinc occurred in sorbed form in six pH neutral rivers.

In the aquatic environment, zinc partitions to sediments or suspended solids in surface waters through sorption onto hydrous iron and manganese oxides, clay minerals, and organic material. Reservoirs located downstream from lead-zinc mining and milling areas were found to contain higher concentrations of zinc than reservoirs in other areas, and the zinc was more highly concentrated in reservoir bottom sediments than in the surrounding soils (Pita and Hyne 1975). In addition, the zinc content in sediment closely correlated with the depth, organic content, and clay content of the sediments. Phosphates and iron hydroxides affect the transfer of metals (including zinc) from river water to the sediments, according to a study by Houba et al. (1983). In this study, zinc was bound predominantly to carbonate and amorphous matter (iron, aluminum, and manganese hydroxides). In addition, mobile components of naturally occurring organic matter contributed to the increase in the metal hydroxide-bound fraction.

The transport of zinc in the aquatic environment is controlled by anion species. In natural waters, complexing agents, such as humic acid, can bind zinc. The stability of zinc complexes depends on the pH of the water and the nature of the complex. The dissociation of the complex may determine the amount of free zinc ions in solution. Zinc-humic acid complexes may be 50% dissociated at pH 5.5 and the dissociation rate may be higher as the pH decreases (Guy and Chakrabarti 1976). Therefore, as the pH of the water decreases, the concentration of zinc ions in the water phase increases at the same rate as that of the release of zinc from the sediment. The magnesium found in the silicate minerals of igneous rocks is often replaced with the divalent zinc ion; consequently, weathering of this zinc-containing bedrock gives rise to Zn^{+2} in solution. The hydrated cation is the dominant form when the pH is ≤9 (EPA 1979d).

The tendency of zinc to be sorbed is affected not only by the nature and concentration of the sorbent but also by pH and salinity (EPA 1979d). Zinc tends to sorb more readily at a high pH (pH >7) than at a low pH (EPA 1979d). Desorption of zinc from sediments occurs as salinity increases (Helz et al. 1975), apparently because of displacement of the adsorbed zinc ions by alkali and alkaline earth cations, which are abundant in brackish and saline waters (EPA 1979d). In column leaching tests with sediment collected from the banks of the Rhone River, the presence of dissolved organic matter and pH was found to be the factors controlling the adsorption and mobility of zinc (Bourg and Darmendrail 1992).

A small fraction of zinc will exist in the aquatic phase as soluble inorganic zinc compounds (e.g., zinc chloride, zinc sulfate). Soluble inorganic zinc compounds hydrolyze in solution, forming zinc hydroxide precipitates. Hydrolysis may lower pH, but the buffering action present in most natural water prevents a significant alteration in pH. The precipitation of zinc hydroxide and zinc carbonate was studied by Patterson et al. (1977), who found that zinc hydroxide precipitates faster than zinc carbonate. Zinc carbonate is soluble in pure water at 25 °C at concentrations of ≤107 mg zinc/L. The hydroxide is soluble only at concentrations of ≤0.2 mg zinc/L. As a result, some of the inorganic forms of zinc that are expected to be present in water are basic carbonate ($Zn_2[OH]_2CO_3$), hydroxide ($Zn[OH]_2$), and silicate (Zn_2SiO_4) (Florence 1980; NAS 1977). When the pH is ≥8, most of these compounds will precipitate; however, as the pH decreases, more and more of these compounds will dissolve and remain in the water phase (EPA 1979d).

The effect of pH on the mobilization of zinc in a few highly acidic clean lakes has been studied (Sprenger et al. 1987; White and Driscoll 1987). In these lakes, in which the pH was ≤3.6, concentrations of zinc were elevated in the water column, and the concentration of zinc in the upper layer of sediment was

substantially lower than values reported for other lakes at higher pH values. The relatively higher concentration of zinc in the water column compared to the sediment may be the result of lower adsorption of zinc on oxide surfaces due to low pH, solubilization of inorganic zinc from the sediment layer, and the dissociation of bound organic complexes of zinc present in the sediment and their subsequent release into the water phase.

The precipitation of zinc sulfide affects the mobility of zinc in reducing environments, especially when hydrogen sulfide is formed. The precipitation of the hydroxide, carbonate, or basic sulfate may become more significant at high concentrations of zinc. Hesterberg et al. (1997) reports that zinc (hydr)oxides and not sulfides are the dominant species in aquifers solids under reducing conditions. The hydroxides and hydrous oxides of iron and manganese are often components of the clay fraction of sediments and often exist as coatings on the surfaces of other minerals (NAS 1977). Zinc may coprecipitate with hydrous oxides when reduced iron or manganese oxides are oxidized. As the new solids are formed, they can trap various ions in their crystal lattices (EPA 1979d).

Soil. The redox status of the soil may shift zinc partitioning. Reductive dissolution of iron and manganese (hydr)oxides under suboxic conditions release zinc into the aqueous phase; the persistence of suboxic conditions may then lead to a repartitioning of zinc into sulfide and carbonate solids. Bostick et al. (2001) describe zinc speciation in contaminated wetland soil that undergoes seasonal flooding. In dry oxidized soils, the authors found that zinc was associated with (hydr)oxide phases, while in flooded systems, zinc was associated with sulfides and carbonates. Reversible change occurred with flooding from dry soil. However, a small fraction of zinc became recalcitrant with (hydr)oxides fraction.

Zinc sorbs strongly onto soil particulates. Little water-soluble and exchangeable heavy metals were found in soil irrigated with raw waste water (Schalscha et al. 1982). Although considerable amounts of metals were added to the soil in soluble and exchangeable forms during waste-water irrigation, they were converted into the less chemically active forms (i.e., organically bonded and inorganic precipitates). Further examination showed that zinc accumulation in soil resulting from waste disposal occurred primarily as inorganic precipitates.

The mobility of zinc in soil depends on the solubility of the speciated forms of the element and on soil properties such as cation exchange capacity, pH, redox potential, and chemical species present in soil; under anaerobic conditions, zinc sulfide is the controlling species (EPA 1980d; Kalbasi et al. 1978). Since zinc sulfide is insoluble, the mobility of zinc in anaerobic soil is low. In a study of the effect of pH

on zinc solubility, Saeed and Fox (1977) showed that, when the pH is <7, an inverse relationship exists between the pH and the amount of zinc in solution. As negative charges on soil surfaces increase with increasing pH, additional sites for zinc adsorption are activated and the amount of zinc in solution decreases. The active zinc species in the adsorbed state is the singly charged zinc hydroxide species (i.e., $Zn[OH]^+$) (Sanders and Kherbawy 1987). Other investigators have also shown that the mobility of zinc in soil increases at lower soil pH under oxidizing conditions and at a lower cation exchange capacity of soil (Bergkvist et al. 1989; Hermann and Neumann-Mahlkau 1985; Tyler and McBride 1982). On the other hand, the amount of zinc in solution generally increases when the pH is >7 in soils high in organic matter. This is a result of the release of organically complexed zinc, reduced zinc adsorption at higher pH, or an increase in the concentration of chelating agents in soil (Saeed and Fox 1977). For calcareous soils, the relationship between zinc solubility and pH is nonlinear. At a high pH, zinc in solution is precipitated as $Zn(OH)_2$, zinc carbonate ($ZnCO_3$), or calcium zincate (Saeed and Fox 1977). Clay and metal oxides are capable of sorbing zinc and tend to retard its mobility in soil. Warwick et al. (1998) studied the mobility of zinc ions in sand. Zinc was more mobile at pH 4 than at pH 6.5 as a consequence of sorption. Goethite (i.e., iron oxyhydroxide) caused a greater decrease in mobility, and increased retardation was also observed with humic acid.

Distribution constants (K_d=concentration of sorbed zinc/concentration of zinc in solution) for zinc in soil range widely from 0.1 to 8,000 L/kg (or mL/g) (Baes and Sharp 1983; Bunzl and Schimmack 1989; Gao et al. 1997; Gerritse et al. 1982; Janssen et al. 1997). K_d values of 100±770 mL/g for sandy loam soil and 0.2±4 mL/g for sandy soils were reported by Gerritse et al. (1982). K_d values ranging from 0.1 to 8,000 mL/g were reported by Baes and Sharp (1983). K_d values for zinc of 140 and 41 L/kg were determined for the O-horizon (organic layer) and E-horizon (silty sand), respectively, of a podzol forest soil (Bunzl and Schimmack 1989). Field-based K_p ranged from 6 to 6,762 L/kg for 20 Dutch agricultural soils (Janssen et al. 1997). K_d values for nine soils treated with sewage sludge supernatant ranged from 0.034 to 1.359 L/g at pH 4.5 while at pH 6.5, K_d values ranged from 0.425 to 2.896 L/g (Gao et al. 1997).

Zinc in a soluble form (e.g., zinc sulfate) is moderately mobile in most soils. However, relatively little land-disposed zinc at waste sites is in the soluble form. Thus, mobility is limited by a slow rate of dissolution. Consequently, movement towards groundwater is expected to be slow unless zinc is applied to soil in soluble form (such as in agricultural applications) or accompanied by corrosive substances (such as in mine tailings) (EPA 1980d). Yet, soil conditions not suitable for zinc sorption may lead to leaching. Low pH (pH <7) and high ionic strength of the leaching solution favor desorption (EPA 1987c; Saeed and Fox 1977).

Consequently, zinc primarily remains in recalcitrant, immobile forms in contaminated soils (Chlopecka et al. 1996; Kabala and Singh 2001; Kaminiski and Landsberger 2000b; Ma and Rao 1997a). Ma and Rao (1997) studied the chemical fractionation of zinc in nine soils from various U.S. locations contaminated by agriculture and industrial activities. Zinc was found to be concentrated in the residual (or recalcitrant) fraction (range, 55.8–97.6%), which reflected greater tendency of zinc to become unavailable once in soils. However, some zinc was found in exchangeable and carbonate fractions at levels ranging from 0.73 to 25%, which suggests that some zinc may be available to plants. In soil from East St. Louis, Illinois, an area heavily contaminated with metals, sequential extraction analysis of soil revealed that the largest fraction of zinc was partitioned in the iron-manganese oxide fraction (47.2%) followed by carbonate (37.9%) and organic (14.1%) and exchangeable (0.8%) fractions (Kaminiski and Landsberger 2000b). Kabala and Singh (2001) reported that water-soluble zinc was present in only very small amounts (<1%) in most contaminated soils. However, concentrations of exchangeable zinc were significantly higher in surface horizons (4–19% of total zinc) than in subsurface layers. In subsurface horizons of the studied soils, zinc was concentrated in the residual (or recalcitrant) fraction. The percentage of residual zinc ranged from 45% in silty soils to 94% in clay-loam soil. The nonresidual fractions prevailed only in the surface horizons in both contaminated and uncontaminated soil (65–91% of total zinc) (Kabala and Singh 2001). Soils from Southwestern Poland subjected to severe metal contamination contained zinc at concentrations ranging from 20 to 10,000 mg/kg (Chlopecka et al. 1996). Acidic soils (pH<5.6) contained a greater fraction of exchangeable zinc, while for other soils (pH>5.6), zinc was found primarily in the oxide and residual (or recalcitrant) fractions with moderate amounts in the organic, carbonate, and exchangeable forms.

Zinc is an essential nutrient and occurs in the tissues of organisms, even at normal ambient water and soil concentrations. Zinc can accumulate in freshwater animals at 51–1,130 times the concentration present in the water (EPA 1987c). Microcosm studies indicate, in general, that zinc does not biomagnify through food chains (Biddinger and Gloss 1984; EPA 1979d; Hegstrom and West 1989). Furthermore, although zinc actively bioaccumulates in aquatic systems, biota appears to represent a relatively minor sink compared to sediments. Steady-state zinc bioconcentration factors (BCFs) for 12 aquatic species range from 4 to 24,000 (EPA 1987c). Crustaceans and fish can accumulate zinc from both water and food. A BCF of 1,000 was reported for both aquatic plants and fish, and a value of 10,000 was reported for aquatic invertebrates (Fishbein 1981). The order of enrichment of zinc in different aquatic organisms was as follows (zinc concentrations in μg/g dry weight appear in parentheses): fish (25), shrimp (50), mussel (60), periphyton (260), zooplankton (330), and oyster (3,300) (Ramelow et al. 1989). The high

enrichment in oysters may be due to their ingestion of particulate matter containing higher concentrations of zinc than ambient water. Other investigators have also indicated that organisms associated with sediments have higher zinc concentrations than organisms living in the aqueous layer (Biddinger and Gloss 1984). With respect to bioconcentration from soil by terrestrial plants, invertebrates, and mammals, BCFs of 0.4, 8, and 0.6, respectively, have been reported. The concentration of zinc in plants depends on the plant species, soil pH, and the composition of the soil (Dudka and Chlopecka 1990; Rudd et al. 1988). Plant species do not concentrate zinc above the levels present in soil (Levine et al. 1989).

6.3.2   Transformation and Degradation

As an element, zinc does not degrade in the environment. Degradation of an element is a nuclear process by definition, and stable elements, such as zinc, typically undergo such processes only at insignificant rates in the environment. Zinc can change from one form to another, sometimes reversibly, in numerous chemical reactions that can proceed under a wide range of common environmental conditions.

6.3.2.1   Air

The chemical interaction of zinc compounds in the atmosphere may change the anionic speciation of the compound. Atmospheric interactions are greatest for particles with small aerodynamic diameters (Fishbein 1981). Zinc is found in the atmosphere at the highest concentrations in the smallest particles (Fishbein 1981). Atmospheric emissions of zinc, consisting primarily of zinc sorbed to submicron particulate matter in the form of zinc oxide (ZnO), are expected to dissipate quickly as a result of deposition to soil and surface waters (EPA 1980d).

In the atmosphere, zinc-bearing particles may undergo chemical transformation before deposition. The association of zinc particles in aerosols in Arizona was studied, and five zinc-bearing particles were identified with an automated scanning electron microscope (Anderson et al. 1988). These particles, in decreasing order of concentration in the aerosol, were zinc sulfide (ZnS), ferrous zinc (Fe_xZn_y), zinc phosphides (Zn_3P_2), zinc chloride ($ZnCl_2$), and metallic zinc (Zn). The presence of zinc sulfide in an area adjacent to mining and smelting activities was not unanticipated, but no conclusion regarding the speciation of zinc in the atmosphere could be drawn from this investigation. However, the relative concentration of zinc ions in rainwater from a rural area was approximately 10 times higher than in

airborne particulates (Aten et al. 1983). This finding suggests that zinc sulfide in the atmosphere is oxidized to a more water-soluble form, zinc sulfate.

6.3.2.2 Water

Zinc is in the +2 form in aqueous solution and exhibits amphoteric properties; zinc metal and compounds dissolve in acids to form hydrated Zn^{+2} cations and in strong bases to form zincate anions, which are hydroxo complexes, such as $[Zn(OH)_3]^-$, $[Zn(OH)_4]^{2-}$, and $[Zn(OH)_4(H_2O)_2]^{2-}$ (EPA 1979d; O'Neil et al. 2001). However, at the pH of most natural waters, the formation of anionic zinc species is not likely.

A small part of the available zinc may partition into the aquatic phase through the formation of soluble zinc chloride and sulfate compounds. These compounds hydrolyze in solution to form the hydroxide or hydrated zinc oxide precipitate with a resultant decrease in pH. The decrease in pH can increase the solubility of zinc hydroxide and increase the zinc concentration in water. However, the buffering action of most natural waters prevents any significant change of pH due to the hydrolysis reactions. As a result, in the water phase, the solubility of its carbonate and hydroxide is likely to control the availability of zinc. It was reported by Patterson et al. (1977) that $Zn(OH)_2$ precipitates faster than $ZnCO_3$. Zinc is not directly affected by changes in Eh; however, the valences and reactivity of ligands reacting with zinc are affected by Eh. Zinc is an active reducing agent for many metal ions such as iron (Fe^{+3}) and permanganate (MnO_4^{-2}) ions (Stokinger 1981). As a result of the reducing reactions, the manganese oxides and ferric salts may precipitate and, in the process, may entrap soluble zinc in the precipitate, thereby reducing the zinc concentration in the water phase.

Because alkyl zinc compounds are unstable in water and oxygen, biomethylation of zinc compounds in aquatic ecosystems probably does not occur (EPA 1979d). Insoluble zinc compounds (e.g., zinc oxide) are solubilized indirectly under anaerobic conditions with reduction of iron sulfides, which reduces the solution pH (Couillard et al. 1994; Francis and Dodge 1988). No evidence was found that photolysis in the aquatic environment significantly affects the fate of zinc compounds.

6.3.2.3 Sediment and Soil

Zinc undergoes reactions in sediment and soil involving precipitation/dissolution, complexation/dissociation, and adsorption/desorption. These reactions are controlled by the pH, redox potential (Eh), the

concentration of zinc ions and other ions in the soil pore water, the number and type of adsorption sites associated with the solid phase, and the organic ligands present that are capable of forming complexes with zinc. In acidic sediments and soils, more zinc is available in ionic forms, and cation exchange processes influence its fate. Depending on the nature and concentrations of other mobile metals in sediments and soils, competition for the binding sites probably occurs. In the absence of suitable binding sites, zinc may be mobilized (ICF 1986). In alkaline soils, the chemistry of zinc is dominated by interactions with organic ligands. The ecological toxicity of sediment is complex and appears to be correlated to the ratio of zinc to acid volatile sulfide (Berry et al. 1996; Di Toro et al. 1992; Sibley et al. 1996).

Biological degradation of zinc complexes in soil is necessary for the normal operation of ecosystems to facilitate the recycling of zinc from litter, feces, and dead organisms. In some environments, bacteria and fungi are able to oxidize zinc sulfide producing zinc sulfate, which will solubilize in the soil solution (WHO 2001).

6.3.2.4 Other Media

During composting of organic wastes, zinc remains in mobile and bioavailable forms. Zinc carbonates are formed, although not at the expense of zinc sulfide levels, which remain unaltered during the composing process (Ciba et al. 1997). No further data were located in the literature for the transformation and degradation of zinc in other media.

6.4   LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

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

6.4.1   Air

Zinc concentrations in air are relatively low and fairly constant except near sources such as smelters. Average atmospheric concentrations of zinc resulting from releases from automobiles, fuel combustion, incineration, soil erosion, and industrial, commercial, and construction activity throughout the United States generally are <1 μg/m^3 (EPA 1980d; Lloyd and Showak 1984). In 1990, the median concentration of zinc in air samples collected across Minnesota was 0.012 μg/m^3 (maximum, 0.187 μg/m^3) (Pratt et al. 2000). At six measurement sites in Columbus, Ohio, the mean atmospheric particulate concentration of zinc for samples collected in 1989 was 0.01±0.01 μg/m^3 (Spicer et al. 1996). Data on zinc concentrations in New York City during 1972–1975 show that the average atmospheric zinc concentration ranged from 0.293 to 0.380 μg/m^3 annually (Lioy et al. 1978). An average ambient zinc concentration of 0.127 μg/m^3 (concentration range, 0.027–0.500 μg/m^3) was determined from analyses of particulate samples collected at nine air monitoring sites in the San Francisco Bay area (John et al. 1973). The concentrations of zinc in atmospheric samples collected from seven cities in the United States during 1968–1971 ranged from 0.17 to 0.67 μg/m^3, whereas the concentrations at two rural sites ranged from 0.02 to 0.16 μg/m^3 (Saltzman et al. 1985). The concentrations of zinc during 1977–1979 from the National Air Surveillance Networks were reported by Evans et al. (1984). The arithmetic mean zinc concentrations in urban areas in the United States ranged from 0.02 to 0.16 μg/m^3, whereas the concentrations in nonurban areas ranged from 0.01 to 0.05 μg/m^3. The geometric mean concentrations of zinc from three urban areas in New Jersey monitored in 1981–1982 ranged from 0.07 to 0.59 μg/m^3, whereas the concentrations at a rural site ranged from 0.02 to 0.06 μg/m^3 (Daisey 1987). Davidson et al. (1988) measured the atmospheric zinc concentrations at Great Smoky Mountains and Olympic National Parks where crustal weathering, sea spray, and long-range transport of zinc were likely to influence concentrations. The average atmospheric concentrations of zinc were 0.0033 and 0.0089 μg/m^3 for Great Smoky Mountains in 1979 and Olympic National Parks in 1980, respectively. The reported concentration range of zinc in air at remote sites (arctic) was <0.003–0.027 μg/m^3 (Barrie and Hoff 1985; Duce et al. 1975; Zoller et al. 1974). In aerosol samples of the lower troposphere collected over the Southern Bight of the North Sea between September 1988 and October 1989, the average zinc concentration was 0.067 μg/m^3 (standard deviation, 0.054 μg/m^3; range, 0.003–0.22 μg/m^3; n=108 samples) (Injuk et al. 1992). The concentration of atmospheric zinc is usually lower in winter than in summer (Barrie and Hoff 1985; Daisey 1987).

Indoor air from other regions of the world has been reported to contain zinc in particulate matter at low levels. In 1991, household dust sampled from Bahrain in Persian Gulf region contained zinc at a concentration of 64.4 μg/g (Akhter and Madany 1993). As part of the Southeastern Brazil Indoor Air

Quality Study (SEBIAQS) in the summer of 1993, indoor and outdoor air samples were collected at

12 sites in the cities of São Paulo and Rio de Janeiro, Brazil. Indoor air particulate samples had higher

levels of zinc than outdoor samples. The concentration of zinc in indoor air particulates from São Paulo

and Rio de Janeiro, Brazil were 0.046–0.30 and 0.036–0.38 $\mu g/m^3$, respectively, while outdoor samples

ranged from not detected to 0.23 and from 0.05 to 0.29 $\mu g/m^3$, respectively (Miguel et al. 1995).

Although data are sparse, higher-than-background concentrations have been reported near iron- and steel-

producing factories and zinc, lead, and copper smelters. During zinc smelting operations, concentrated

zinc ore goes through a roasting procedure to convert zinc sulfide to zinc oxide. This process accounts

for a large portion of the total atmospheric zinc emission during primary production (EPA 1980d). About

1.5 miles from a smelter in Kellogg, Idaho, Ragaini et al. (1977) detected high annual mean

concentrations of zinc in ambient air of 5 $\mu g/m^3$. The 24-hour values for zinc ranged from 0.27 to

15.7 $\mu g/m^3$; the average lead and cadmium concentrations at this smelter site were 11 and 0.8 $\mu g/m^3$,

respectively, indicating severe environmental pollution. Higher concentrations of zinc in the vicinity of a

copper smelter than in reference areas were also reported by Patterson et al. (1977).

6.4.2   Water

In general, zinc is more concentrated in the sediments of streams and rivers than in the water column. It

is reported by NAS (1977) that zinc is probably detectable in 75% of all water samples from various

locations. The zinc background concentrations in surface waters are usually <50 $\mu g/L$ (EPA 1980d), but

concentrations in surface waters and groundwater can range from 0.002 to 50 mg/L (NAS 1977).

Table 6-4 summarizes the typical concentrations of dissolved zinc in rivers of the United States (Shiller

and Boyle 1985). The concentration of dissolved zinc in water from three Adirondack lakes was highest

for low pH waters (Heit et al. 1989). Lake water from Darts Lake (pH 5.1–5.4) contained 7.9 ng zinc/mL

while Moss Lake, a lake with variable acidity (pH 5.8–6.7), contained zinc at 2.9 ng/mL and Rondoxe

Lake, a neutral lake (pH 6.5–6.8), contained 2.5 ng zinc/mL.

In many locations (e.g., New England, the southeast, the Missouri River basin, the Rio Grande River

basin, and the Upper Colorado River basin), higher-than-background concentrations of zinc are common

and appear to be correlated with mining activities in these areas and/or geological areas rich in zinc (EPA

1980d). However, in all river basins, there are some locations with zinc concentrations of 0.1–1.0 mg/L

(EPA 1980d). In the Upper Rio Grande River, the dissolved zinc concentration upriver of Willow Creek,

which drains a metal mining district, was approximately 2–3 $\mu g/L$. Immediately downstream of the

Table 6-4. Dissolved Zinc in Rivers of the United States[a]

River[b]	Date[c]	pH	Zinc (µg/L at 20 °C)[d]
Ohio Valley			
Allegheny (Pittsburgh, PA)	May 1984	6.86	1.89, 2.02
Monongahela (Pittsburgh, PA)	May 1984	7.22	2.54, 2.87
Ohio (Wheeling, WV)	May 1984	7.34	3.19, 3.19
Muskingum (Zanesville, OH)	May 1984	7.55	1.04, 1.24
Muskingum (Marietta, OH)	May 1984	7.66	0.63, 0.63
Kanawha (Winfield, WV)	May 1984	7.4	0.33, 0.35
Big Sandy (Louisa, KY)	May 1984	7.15	0.33,0.33
Ohio (Greenup Dam)	May 1984	7.42	0.78, 0.91
Sciotto (Portsmouth, OH)	May 1984	7.87	1.30, 1.43
Little Miami (Milford, OH)	May 1984	8.1	0.85, 1.04
Licking (Alexandria, KY)	May 1984	7.63	0.07
Great Miami (Cleves, OH)	May 1984	8.0	4.24, 4.30
Whitewater (Elizabethtown, OH)	May 1984	7.95	0.16
Ohio (Warsaw, KY)	May 1984	7.45	0.39, 0.42
Kentucky (Lockport, KY)	May 1984	7.28	0.12, 0.15
Ohio (Cannelton Dam)	May 1984	7.27	0.61
Green (Beach Grove, KY)	May 1984	7.32	0.16, 0.16
Wabash (New Harmony, IN)	May 1984	8.1	0.49
Cumberland (Barkley Dam)	May 1984	7.44	0.10, 0.10
Tennessee (Kentucky Dam)	May 1984	7.10	0.12, 0.12
Ohio (Mound City, IL)	May 1984	7.49	0.29, 0.29
Mississippi River			
Mississippi (Cape Girardeau, MO)	May 1984	7.70	0.19, 0.23
Mississippi (Baton Rouge, LA)	Sept 1983	8.1	0.10, 0.12
Mississippi (Baton Rouge, LA)	Apr 1984	7.72	0.18, 0.19
Atchafalaya (Krotz Springs, LA)	Apr 1984	7.6	0.18
Other U.S. rivers			
Connecticut (Old Saybrook, CT)	Apr 1983	7.1	0.91, 1.04
Mullica	Aug 1983	5.81	2.54, 2.61
Merrimack (West Newbury, MA)	Feb 1983	6.73	13.04. 13.04
Vermilion, (Lafayette, LA)	Apr 1984	7.1	0.25, 0.27
Delaware (West Trenton, NJ)	Apr 1984	7.38	3.91, 3.98
Delaware (Philadelphia, PA)	Apr 1984	7.05	13.04, 15.65
Schuykill (Philadelphia, PA)	Apr 1984	7.58	4.56, 4.89

Table 6-4. Dissolved Zinc in Rivers of the United States[a]

River[b]	Date[c]	pH	Zinc (µg/L at 20 °C)[d]
Susquehanna (Holtwood, PA)	Apr 1984	7.54	0.78, 0.85
Potomac (Great Falls, MD)	Apr 1984	7.75	0.54, 0.55

[a]Source: Shiller and Boyle 1985
[b]Post office state abbreviations are used.
[c]Apr = April; Aug = August; Feb = February; Sept = September
[d]Calculated from nmol/kg using density of water at 20 °C (0.99707 g/mL) and zinc molecular weight of 65.39 g/mole.

Willow Creek confluence, zinc concentrations were >20 µg/L and elevated concentrations occurred for the next 100 km (Taylor et al. 2001). The concentrations of zinc in water samples from Whitewood Creek, South Dakota, were measured by Hale (1977). The samples were collected upstream from the discharge of a local mining company. In 42 analyses, zinc concentrations ranged from <0.004 to 0.048 mg/L with a mean concentration of 0.018 mg/L. May et al. (2001) reported that water samples analyzed in 1996 from this contaminated watershed contained zinc at concentrations of 2.4–21 and 3.8–30 µg/L for filtered and unfiltered samples, respectively.

The average levels of dissolved zinc in water from Lakes Superior, Erie, and Ontario were 277, 87, and 160 ng/L, respectively, for samples collected between 1991 (Lake Superior) and 1993 (Lakes Ontario and Erie) (Nriagu et al. 1996). Coale and Flegal (1989) reported that concentration of dissolved zinc in water from Lakes Erie and Ontario ranged from 3×10^{-6} to 1.1×10^{-4} mg/L. In summer, there is a marked depletion of zinc in the epilimnion (i.e., area of warmest water) of Great Lakes off-shore waters, which may be attributed to biological processes (Nriagu et al. 1996). Groundwater from a shallow alluvial aquifer beneath a major urban center (Denver, Colorado) contained dissolved zinc at a median concentration of 3 µg/L (range, 2–28 µg/L) (Bruce and McMahon 1996).

Scudlark et al. (1994) reported that the average concentration of zinc in water from the Chesapeake Bay was 1.21±0.95 µg/L (n=5) for samples collected from 1990 to 1991. The median concentration of zinc in the Hudson River estuary decreased from 200 nM (1.6 ng/L) in 1974 to approximately 25 nM (13 ng/L) in 1997 (Sañudo-Wilhelmy and Gill 1999). The declining levels of zinc and other metals is a result of the decreased metal flux to the estuary from sewage effluents. Zinc concentrations in remote regions of the Atlantic Ocean ranged from 0.023 to 0.097 µg/L in the Northeast region and averaged 0.004 µg/L in the Northwest region (Helmers and Schrens 1995). Yeats (1988) reported that the concentrations of dissolved zinc in ocean water from the Sargasso Sea and Northeast Pacific were 0.3–3.0 nM (20–200 ng/L) in 1984 and 3.6–9.2 nM (240–600 ng/L) in 1981, respectively. Seawater from lagoons of the Gulf of Mexico contained average dissolved zinc concentrations of 2.37, 5.12, and 9.76 µg/L for locations at Alvarado, San Andres, and Sedue (in Mexico), respectively (Vazquez et al. 1995). The concentration of zinc in surficial seawater from the Indian River lagoon (Florida) ranged from 0.01 to 6.6 µg/L (average, 0.8±1.4 µg/L) in 1992 (Trocine and Trefry 1996).

Zinc concentration in precipitation from remote regions of the Atlantic Ocean ranged from 0.359 to 3.93 µg/L (Helmers and Schrens 1995). Heaton et al. (1990) reported that precipitation collected from three locations Rhode Island between 1985 and 1988 contained zinc at median concentration of 4.5 ppb

(n=269). Levels of zinc were higher in samples collected in warm periods (5.8 ppb) versus cold periods (3.7 ppb). Nearly all zinc was dissolved in these samples. Trace amounts of zinc were measured in cloud water (n=3; range, <10–43 µg/L) collected from Whiteface Mountain (Adirondacks Region, New York) in the summer of 1987 (Khwaja et al. 1995). Municipal waste incineration was the primary source of zinc in these wet deposition samples. Snow near an expressway in Montréal, Québec, Canada, contained zinc at average concentrations of 0.143, 0.33, 0.034, and 0.029 mg/L at 15, 20, 125, and 150 meters from the roadway, respectively (Loranger et al. 1996). Higher zinc concentrations near expressway were the result of road dust from tire abrasion.

Available data suggest that zinc concentrations in drinking water are far less than levels required to meet a daily intake level of 11 mg/day (assuming an adult water consumption of 2 L/day) (IOM 2002). Concentrations of zinc in drinking water can be higher than levels in surface waters. Concentrations of 0.002–1.2 mg/L were detected in 77% of 1,577 surface water samples while levels of 0.003–2.0 mg/L were found in 380 drinking water samples (NAS 1977). Higher concentrations in drinking waters are a result of water treatment and of contamination from plumbing of the water distribution system.

Zinc was found in drinking water at levels as great as several mg/L as a result of galvanized pipes and tanks in alkaline-water distribution systems. Drinking water samples from galvanized pipe plumbing systems in Seattle, Washington, contained zinc concentrations of 0.128–1.279 mg/L; these levels were >10 times higher than those in homes with copper pipe plumbing systems (Sharrett et al. 1982a). Forty-three tap-water samples collected from homes in Dallas, Texas and analyzed for trace metals reported maximum, minimum, median, and average zinc concentrations of 0.049, 0.005, 0.011, and 0.0124 mg zinc/L, respectively (NAS 1977). High zinc concentrations in these water samples were believed to be due to the household plumbing. In a study investigating associations between inorganic constituents of drinking water and cardiovascular diseases, Greathouse and Osborne (1980) collected and analyzed tap water samples in 35 geographic areas in the United States; 100–110 tap-water samples were collected from each area. The maximum, minimum, and mean concentrations were 1.447, 0.025, and 0.144 mg zinc/L, respectively. Seventy-five percent of the zinc values were below 0.236 mg/L. Other investigators have attributed the higher concentrations of zinc in household tap waters, compared to finished drinking water, to distribution and transmission lines (Maessen et al. 1985; Ohanian 1986; Schock and Neff 1988).

The median concentration of zinc in leachate from municipal landfills in the United States ranged from 0.68 to 1.7 mg/L with a high concentration of 250 mg/L (Roy 1994).

6.4.3   Sediment and Soil

Zinc is found in soils and surficial materials of the conterminous United States at concentrations between <5 and 2,900 mg/kg, with a mean of 60 mg/kg (Schacklette and Boerngen 1984). Zinc concentrations measured across the United Stated ranged from <5 to 400 mg/kg and from <10 to 2,000 mg/kg, with corresponding means of 36 and 51 mg/kg in cultivated and uncultivated subsurface soils, respectively (Connor and Shacklette 1975); however, these differences in zinc concentration may be attributed to differences in the soils prior to use (and not to cultivation). The sampling survey was designed to determine zinc concentrations of surficial materials unaltered from their natural condition. Chen et al. (1999) determined the baseline concentration of zinc in 448 representative Florida surface soils as part of the Florida Cooperative Soil Survey Program. Baseline soil samples represent natural elemental concentrations without human influence. The mean concentration of zinc was 8.35±13.8 mg/kg (range, 0.9–169 mg/kg) in archived soil samples from this study.

Soils near highways and smelters contained high zinc concentrations as a result of deposition of zinc released in tire abrasion and stack emissions (EPA 1980d; Norrström and Jacks 1999). Urban alluvial soils from New Orleans, Louisiana had higher levels of zinc as a result of highway traffic (130 µg/g) than freshly deposited lower Mississippi River delta spillway alluvium (11.1 µg/g) (Mielke et al. 1999, 2000).

A study was designed by Hutchinson and Wai (1979) to investigate the distribution of cadmium, lead, and zinc in the soil and vegetation at two reclaimed waste dumps from phosphate ore mines in southeastern Idaho. Zinc concentrations in the soil of the waste dumps averaged from 443±210 to 1,112±124 mg/kg. These values were high compared to those found in the control plot (54±16 mg/kg). Zinc concentrations in vegetation from the reclaimed waste dumps were also high compared to the control plot. Moderate-to-high levels of zinc contamination were found in leafy vegetables (lettuce) and their supporting soil in a zone with a 0–5-km radius around a copper smelter (Beavington 1975). The mean concentrations of zinc in 17 soil samples and 12 lettuce samples collected in this zone were 229±17 and 316±64 mg/kg dry weight, respectively. Significant relationships were found between the distance from the smelter and the levels of easily extractable zinc in the soil, and between the distance from the smelter and the content of zinc in herbage. The concentration of zinc in soil at the Palmerton zinc smelter site in eastern Pennsylvania was determined 6 years after zinc smelting was terminated in 1980 (Storm et al. 1994). Levels in soils were highest (4,160 mg/kg) at sites close to the former smelter and decreased with distance. Zinc concentrations in urban top soils from the western half of East St. Louis, Illinois (a city with historical industrial activities such as smelting of nonferrous metals) ranged from 79 to 10,360 µg/g

with an average concentration of 1,034 µg/g (Kaminski and Landsberger 2000). Concentrations of zinc in soil irrigated with waste water or river water were measured by Schalscha et al. (1982). The total concentration of zinc in waste water-treated soils was 228 mg/kg. The total concentration of zinc in soils irrigated with river water ranged from 103 to 136 mg/kg.

Soils around galvanized water and electrical transmission towers have been reported to have elevated levels of zinc (Jones and Burgess 1984). Near Peterborough, Ontario, Canada, soil nearest to a galvanized water tower contained zinc at a concentration of 11,480±2,966 µg/g dry weight, while the concentration of zinc in soil 50 meters from the tower was 54±16 µg/g dry weight.

Municipal sludge and municipal incineration ash contain considerably higher levels of zinc than uncontaminated soils (Mumma et al. 1984, 1990, 1991). Therefore, application of sludge and municipal ash to soil will elevate the levels of zinc in these soils. The mean concentrations (mg/kg) of zinc according to four land use types were as follows: agricultural, 25; suburban residential, 75; mixed industrial/residential, 157; and industrial inner urban area, 360 (Haines 1984).

Zinc in water is transported to the sediment in the adsorbed or precipitated phase; the concentration of zinc in sediments of most waters is higher than the zinc concentration in aqueous phase. From 1992 to 1996, streambed sediments samples were collected from 541 locations at more than 50 river basins across the conterminous United States (illustrated in Table 6-5) as part of the National Water-Quality Assessment Program (Rice 1999; USGS 2002). The median zinc concentration in these sediments was 110 µg/g dry weight (range, <4.0–9,000 µg/g dry weight). Samples collected from urban settings were enriched in zinc relative to agricultural or forest settings. The highest median concentration was observed in the Upper Colorado River Basin while the lowest was observed in Central Nebraska Basins (USGS 2002). Bed sediments from the South Platte River basin sampled from 1992 to 1993 contained zinc at concentrations ranging from 82 to 3,700 µg/g dry weight (average, 454 µg/g dry weight) (Heiny and Tat 1997). The highest concentrations were observed near the urban region around Denver, Colorado and in the Rocky Mountains. In 1979–1980, as part of the Apalachicola River Quality Assessment, fine grained sediment (<20 µm particle size) of the Apalachicola River was reported to contain zinc at a median concentration of 70 µg/g dry weight (n=15; range, 20–150 µg/g dry weight) (Elder and Mattraw 1984). Surficial lake sediments from four locations in Rock Mountain National Park contained zinc at mean concentrations ranging from 72±4 to 125±3 µg/g dry weight (Heit et al. 1984). The geometric mean and range of zinc levels in lake sediment from 189 sites in 52 Quebec and Ontario, Canada lakes were 125.2 and 3.0–559.9 µg/g dry weight, respectively (Rowan and Kalff 1993). The concentrations of zinc

Table 6-5. Median Zinc Levels in Bed Sediment from River Basins of the United States[a]

NAWQA study unit[b]	Median concentration of zinc (μg/g dry weight)
Acadian-Ponchartrain (ACAD)	120
Albemarle-Pamlico Drainage (ALBE)	99
Allegheny and Monongahela River Basins (ALMN)	195
Apalachicola-Chattahoochee-Flint River Basin (ACFB)	130
Central Arizona Basins (CAZB)	160
Central Columbia Plateau (CCPT)	82
Central Nebraska Basins (CNBR)	69
Connecticut, Housatonic, and Thames River Basins (CONN)	200
Cook Inlet Basin (COOK)	110
Delaware River Basin (DELR)	290
Eastern Iowa Basins (EIWA)	72.5
Georgia-Florida Coastal Plain (GAFL)	100
Great and Little Miami River Basins (MIAM)	130
Hudson River Basin (HDSN)	180
Kanawha-New River Basin (KANA)	200
Lake Erie-Lake St. Clair Drainage (LERI)	120
Long Island and New Jersey Coastal Drainages (LINJ)	245
Lower Illinois River Basin (LIRB)	88
Lower Susquehanna River Basin (LSUS)	300
Lower Tennessee River Basin (LTEN)	84
Mississippi Embayment (MISE)	91.5
Mobile River and Tributaries (MOBL)	110
Nevada Basin and Range (NVBR)	100
New England Coastal Basins (NECB)	295
Northern Rockies Intermontane Basins (NROK)	108
Oahu (OAHU)	375
Ozark Plateaus (OZRK)	90
Potomac River Basin (POTO)	130
Puget Sound Basin (PUGT)	130
Red River of the North (REDN)	95
Rio Grande Valley (RIOG)	82.5
Sacramento River Basin (SACR)	120
San Joaquin-Tulare Basin (SANJ)	110
Santa Ana Basin (SANA)	160
Santee Basin and Costal Drainages (SANT)	94
South Central Texas (SCTX)	77
South Platte River Basin (SPLT)	180
Trinity River Basin (TRIN)	77.5

Table 6-5. Median Zinc Levels in Bed Sediment from River Basins of the United States[a]

NAWQA study unit[b]	Median concentration of zinc (μg/g dry weight)
Upper Colorado River Basin (UCOL)	940
Upper Illinois River Basin (UIRB)	110
Upper Mississippi Basin (UMIS)	110
Upper Snake River Basin (USNK)	81
Upper Tennessee River Basin (UTEN)	140
Western Lake Michigan Drainage (WMIC)	98
White River Basin (WHIT)	100
Willamette River Basin (WILL)	120
National median	*110*

[a]Source: USGS 2000
[b]( ) = acronym for study unit

in sediments of the upper Columbia River, British Columbia, ranged from 45 to 51 mg/kg, while zinc concentrations in sediments from Lake Roosevelt, Washington were 60–26,840 mg/kg (Johnson et al. 1990). The higher zinc concentrations in lake sediments were due to discharges from a lead-zinc smelter and a refinery. Contaminated sediments in the West Branch of the Grand Calumet River (Indiana/ Illinois), a river system heavily impacted by various industrial activities for many years, were found to contain zinc at concentrations ranging from 325 to 9,281 ppm (mean, 1,270±1,097 ppm) (Cahill and Unger 1993). Sediment samples collected from streams in the Black Hills, South Dakota, an area impacted by gold mining operations, contained zinc at levels ranging from 3.8 to 250 µg/g dry weight (May et al. 2001).

Marine sediments also contain elevated concentrations of zinc with respect to concentrations of zinc in seawater. The concentration of zinc in Hamilton Harbor sediments ranged from 1,050 to 2,900 mg/kg, compared to zinc concentrations of 6–48 µg/L in the aqueous phase (Mayer and Manning 1990). Surficial sediments from the Newark Bay Estuary, Hackensack River, Newark Bay, Arthur Kill, and Kill van Kull contained zinc at mean concentrations of 739.5±243.9, 426±600.5, 489.8±238.1, 769.1±715.2, and 331.3±213.7 ppm, respectively (Crawford et al. 1995). Sediment samples collected from the Hudson River Estuary in 1991 contained zinc at levels of 27–215 and 400–2,500 mg/kg in bottom and suspended sediment, respectively (Gibbs 1994). Marine sediment samples from the border region of Baja California (Mexico) and California (United States) contained zinc at concentration levels ranging from 39 to 188 µg/g dry weight (mean, 68.3 µg/g dry weight) in the fine fraction (<63 µm) of sediment. A relative enrichment of >350% was observed with respect to nonpolluted sediments of the region (Villascusa-Celaya et al. 2000). Marine sediment in coastal areas of Mexico (Pacific Ocean and Gulf of Mexico) was found to contain zinc at mean concentrations ranging from 4.0 to 227.0 µg/g dry weight (Villanueva and Botello 1998). Soto-Jimenez and Páez-Osuna (2001) reported mean concentrations of zinc ranging from 84.3±38.7 to 359±76.5 mg/kg dry weight for marine sediments collected in November 1994 from Mazatlán Harbor, Mexico (southeastern Gulf of California). This harbor receives land runoff and untreated or partially treated industrial, shipping, and domestic effluents from local point sources. During the period of 1984–1985, marine sediment samples were collected from the San Andres lagoon of the Gulf of Mexico, which is located near two industrial ports and industrial effluent is discharged into the lagoon year round. Sediments from this region were found to contain zinc at a concentration of 10.1 mg/kg dry weight (Vasquez et al. 1994).

6.4.4   Other Environmental Media

As part of the National Water Quality Assessment (NAWQA) Program, the concentration of zinc in various species of fish was measured (USGS 2000a, 2000b, 2001). The concentration of zinc in fish fillet sampled from the Lower Tennessee River Basin ranged from 3.0 to 46.0 µg/g dry weight for 79 of 102 positive detections from 1980 to 1998 (USGS 2001). Fish fillets collected from the Clark Fork-Pend Oreille and Spokane River Basins (Washington, Idaho, and Montana) contained zinc at concentrations ranging from 11 to 36 µg/g dry weight (n=15; median 16 µg/g dry weight) in 1998 (USGS 2000b). In the National Contaminant Biomonitoring Program, the geometric mean concentration of zinc in various whole fish was 21.7 mg/kg wet weight (Schmitt and Brumbaugh 1990). Of all fish tested (e.g., bloater, sucker, white perch, bass, catfish, etc.), common carp showed the highest level of zinc. No significant trend in the level of zinc in whole fish was observed during 1978–1984. Blevens and Pancorbo (1986) determined the zinc concentrations in muscle tissue of fish from aquatic systems in east Tennessee, from 1980 to 1984. Mean levels of zinc in fish from Nolichucky and Little Chucky Creeks ranged from 12 to 19 ppm wet weight. Fish from Watauga and Boone Lakes had a range of mean zinc concentrations of 8.3–12 ppm wet weight; in the Holston River Basin, the range of mean concentrations of zinc was 4.6–28 ppm wet weight. The mean concentration of zinc in muscle tissue of tuna (*Thunnus thynnus*) collected from the northwest Atlantic Ocean was 17 µg/g dry weight (range, 12–25 µg/g dry weight) in 1990 (Hellou et al. 1992).

Zinc will not concentrate in fish tissues with exposure to elevated concentrations. The concentration of zinc in yellow perch (*Perca flavescens*) from six acidic lakes in northwestern New Jersey ranged from 26.1 to 66.2 mg/kg dry weight (Sprenger et al. 1988). Although the concentrations of mercury and lead in fish from acidic lakes were higher compared to fish collected from nonacidic lakes, the concentrations of zinc showed no significant difference. Similarly, high concentrations of zinc were not found in white suckers (*Catostomus commersoni*) and brown bullheads (*Ictalurus nebulosus*) collected from two acidic Adirondack lakes in New York (Heit and Klusek 1985). Fish from the Milltown Reservoir Superfund Site in Montana (characterized by elevated concentrations of metals in wetland soils, surface water, and groundwater) contained zinc in whole body tissues at a concentration of 26.3 mg/kg wet weight (Pascoe et al. 1996). Redear sunfish (*Lepomis microlophus*), largemouth bass (*Micropterus salmoides*), and bluegill sunfish (*Lepomis macrochirus*) were collected from storm water ponds and natural lakes and ponds in Orlando, Florida between 1991 and 1992 (Campbell 1994). The mean concentrations of zinc in whole fish collected from storm water ponds were 42.2, 29.99, and 36.1 mg/kg wet weight for redear sunfish, largemouth bass, and bluegill sunfish, respectively. At natural lakes and ponds (controls sites),

the mean concentrations of zinc were 24.83, 21.18, and 30.72 mg/kg wet weight for redear sunfish, largemouth bass, and bluegill sunfish, respectively.

Bivalves and other sessile estuarine organisms are often used as a measure of contamination of estuarine water because they usually contain higher levels of metals than fish. The arithmetic mean concentration of zinc in oysters (*Crassostrea virginica*) from the Mississippi Sound collected in 1988 was 640 mg/kg wet weight (Lytle and Lytle 1990). Oysters collected from the San Andres lagoon (Gulf of Mexico) from 1984 to 1985 contained zinc at a concentration of 3,180 mg/kg dry weight (Vazquez et al. 1994). The mean concentration of zinc in oysters (*C. virginica*) collected from the U.S. coastline of the Gulf of Mexico during 1986–1988 was 2,150 mg/kg dry weight (Presley et al. 1990). In a nationwide mussel watch program, the mean concentrations of zinc in molluscs (*Mytilus edulis*) around the coast of the United States during 1976–1988 ranged from 67 to 3,700 mg/kg dry weight (Lauenstein et al. 1990). Although the concentration on a nationwide basis varied depending on sampling sites, the level of zinc showed little evidence of statistically significant change during 1976–1988. Clams endevors (*Corbicula manilmsis*) collected as part of the Apalachicola River Quality Assessment between 1979 and 1980 contained zinc at a median concentration of 20 µg/g dry weight (range, 2.1–26 µg/g dry weight) (Elder and Mattraw 1984). Blue crabs (*Callinectes sapidus*) from the Quinnipac and Connecticut Rivers (Connecticut), which are mostly harvested for personal consumption, contained zinc in muscle and heltopancreas tissues at concentrations of 31–33 and 27–28 mg/kg wet weight, respectively (Jop et al. 1997).

Vegetation may accumulate higher levels zinc if grown on contaminated soils. Jones et al. (1988) found that corn plants and young corn plants (*Zea mays*) grown beneath and close to a galvanized electrical transmission tower had elevated concentrations of zinc due to corrosion of the zinc protective layer on the steel. Corn seedlings grown in a highly contaminated soil (1,425 µg zinc/g soil) a meter from the tower had zinc concentration in shoots and roots of 484±103 and 1,330±250 µg/g dry weight, respectively. In contrast, seedlings grown in soil 50 meters from tower (67.3 µg zinc/g soil) had zinc concentrations in shoots and roots of 25.3±4.2 and 21.0±2.6 µg/g dry weight, respectively. Bache et al. (1991) found concentrations of zinc were highest in grass samples (*Phleum pratense L.*; *Agropyron repens L.; Bromus inermis L; Phalaris arundinacea L.*) collected immediately adjacent to the a municipal waste incinerator (135.7 µg/g dry weight) compared to grass samples collected upwind or a distance from the incinerator (17.82–73.78 µg/g dry weight). Grasses collected from the Milltown Reservoir Superfund Site in Montana contained zinc at concentrations of 153.7 and 882.1 mg/kg for above- and below-ground samples, respectively (Pascoe et al. 1996). In contrast, control samples from a reference area contained

zinc at concentrations of 71.8 and 36.2 mg/kg for above- and below-ground samples, respectively. Other studies have not shown significant correlations between zinc concentrations in soils and vegetation (Fytianos et al. 2001; Schuhmacher et al. 1998).

Sewage sludge and compost, which may be used in agriculture as a soil amendment, have high levels of zinc. The average concentrations of zinc in municipal solid waste compost and sewage from the United States were found to be 609 and 1,202 mg/kg dry weight, respectively (He et al. 1995). The median concentration of zinc found in residential compost from Toronto, Canada was 190 mg/kg dry weight (range, 100–410 mg/kg dry weight) (Evans and Tan 1998). Biowaste, composed of organic waste products from indoors and outdoors, contained zinc at concentrations of 120 ± 25, 129 ± 13, and 338 ± 58 mg/kg dry matter in the >5 mm, 1–5 mm, and <0.05 mm fractions, respectively (Veeken and Hamelers 2002).

Other environmental concentrations of significance include coal and paint. Coal from the United States was found to contain zinc at a mean concentration of 53 ± 440 ppm (n=7,908; maximum=19,000 ppm) (Finkelman 1999). Zinc was present at a median concentration of 31,101 µg/g (n=31; range, 52–98,056 µg/g) in paint from historic old homes of New Orleans, Louisiana (Mielke et al. 2001).

6.5   GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

General Population. Zinc is essential element needed by the body in small amounts and ranks as one of the most abundant trace metals in humans. Sources of exposure to zinc include ingestion of food, drinking water, food, polluted air, tobacco products, and occupational exposure, with ingestion of food being the primary route of exposure. NAS established the RDA for zinc at 11 mg/day for men and 8 mg/day for women (IOM 2002).

The average daily intake (AVDI) of zinc in humans is on the order of 5.2–16.2 mg zinc/day (Pennington et al. 1986). The dietary intake of an average teenage male has been estimated to be 0.27 mg zinc/(kg/day). Dietary supplements may provide up to an additional 1 mg zinc/(kg/day) (EPA 1980d). In an extensive survey of foods in the total diets of individuals in the United States, conducted by FDA during 1982–1984, the following values for daily zinc intakes (mg/day) were estimated in eight age and sex groups: 6–11-month-old infants, 5.24; 2-year-old children, 7.37; 14–16-year-old girls, 9.90; 14–16-year-old boys, 15.61; 25–30-year-old women, 9.56; 25–30-year-old men, 16.15; 60–65-year-old women, 8.51; and 60–85-year-old men, 12.64 (Pennington et al. 1986). FDA included drinking water in

the total diet. In 1986, the average daily intakes of 40 African-Americans (age 21–65 years old living in Washington D.C. area) were 7.7±0.4 mg for men and 9.1±0.7 mg for women (Ellis et al. 1997). These results are comparable with data from the USDA's Continuing Survey of Food Intakes by Individuals (CSFII) and the National Health and Nutrition Examination Survey (NHANES) III, which reported average daily intakes as follows: NHANES III, 40–49 year old value, male (12.3 mg/day), female (8.5 mg/day); CSFII, >20-year-old value, male (12.9 mg/day), female, (8.3 mg/day). The estimated average daily intakes of zinc were reported to be 14, 11, 14, and 13.2 mg/day in France, Spain, Sweden, and Belgium, respectively (Biego et al. 1998). Using a market basket method, the average daily intakes of zinc for residents of Japan were estimated as 8,700 and 8,500 µg/day for the years 1991 and 1992, respectively (Tsuda et al. 1995).

After a review of the literature, the National Research Council concluded that zinc concentrations in drinking water are generally well below 5 mg/L (NAS 1977). Assuming a daily intake of 2 L of water and an average body weight of 70 kg, a daily intake of <0.14 mg zinc/kg/day from drinking water can be estimated. Based on a body weight of 70 kg, the mean daily intakes of zinc in drinking water for residents of homes with galvanized and copper pipe plumbing systems in Seattle, Washington, were estimated to be 0.017–0.028 and 0.002–0.006 mg/kg/day, respectively (Sharrett et al. 1982b).

Food is the major source of zinc for the general population (EPA 1987c). Zinc is widespread in commonly consumed foods but tends to be higher in those of animal origin, particularly some seafoods (e.g., one serving of oysters will more than meet the daily dietary requirements of zinc) (NAS/NRC 1979). Meat products contain relatively high concentrations of zinc, whereas fruits and vegetables have relatively low concentrations. Meats, fish, and poultry contained an average of 24.5 mg zinc/kg, whereas grains (or cereal products) and potatoes contained 8 and 6 mg/kg, respectively (Mahaffey et al. 1975). Zinc was present in all of the examined food classes. A diet of dairy products, meat, fish, poultry, grains, and cereals provides approximately 77% of the daily zinc intake. Data reported by the Food Safety and Inspection Service of the U.S. Department of Agriculture indicate that zinc was detected in 99.4–100% of the samples of healthy livestock and poultry randomly selected from among the specimens presented for slaughter in 1985–1986. Zinc concentrations in muscle tissue ranged from 0.20 ppm in young turkeys (n=61) to 1.92 ppm in heifers/steers (n=287) (Coleman et al. 1992). In a review of zinc levels in vegetables and other foods and beverages of plant origin, Weigert (1991) reported the following average concentrations (mg/kg): wheat, 41; rye, 13; rice, 8–20; potatoes, 3.51; vegetables, 4.31; fruit, 1.66; mushrooms, 9.7; cocoa, 35; tea, 35; and coffee, 6.7. Zinc is found in onions, peas, and potatoes from Denmark at mean concentrations of 3.4, 3.3–5.5, and 7.9 mg/kg fresh weight, respectively (Bibak et al.

1998a, 1998b; 1999). Zinc has also been detected in wines from Seville, Spain, at concentrations of 0.3–5.40 µg/mL, while concentrations of zinc in sherry wines ranged from 0.12 to 5.08 mg/L (López-Artiguez et al. 1990, 1996). As part of the U.S. FDA's Total Diet Study (TDS), market basket food items from locations in United States were sampled from 1991 through 1999 (FDA 2000). Results from this survey showed the highest amounts of zinc in cereals ranging from a mean of 147 mg/kg for fruit-sweetened cereals to 8.2 mg/kg for corn flakes. Beef and other meat products also included a large amount of zinc, with the highest meat product mean being 81 mg/kg for baked beef chuck roast. In France, the estimated dietary intake of zinc from different foods were determined as follows (µg/day): vegetables, 807; fruits, 143; beverages, 143; cereals, 2,572; fish-crustaceans, 795; meat-poultry-eggs, 8,318; milk-dairy products, 1,127; condiments-sugar-oils, 140; canned foods, 383; and total, 14,429 (Biego et al. 1998). The largest percentage of zinc is from meat-poultry-eggs (58%) followed by cereals (18%) and milk-dairy products (8%).

Federal regulations permit the use of zinc acetate, zinc oxide, and zinc sulfide as components of adhesives, coatings, or rubber packaging materials intended for food contact (FDA 1987b, 1987c, 1987d). Federal regulations also permit the use of zinc chloride, zinc oxide, zinc stearate, and zinc sulfate as GRAS (Generally Recognized As Safe) food additives when they are used "in accordance with good manufacturing practices" (FDA 1987e, 1987f, 1987g, 1987h, 1987i, 1987j). In addition, the use of zinc oxide as a color additive in drugs and cosmetics is also permitted with certain restrictions (FDA 1987a).

Negligible quantities of zinc are inhaled in ambient air. Exposure to airborne zinc is largely occupational through the inhalation of industrial dusts or fumes. Individuals occupationally exposed to metallic zinc and zinc compounds are those involved in galvanizing, smelting, welding, or brass foundry operations. In such operations, zinc as ore or metal and its alloys are often exposed in an oxidizing atmosphere to temperatures near the metal's boiling point of 907 °C. This heating results in the formation of fresh zinc oxide particles (0.2–1.0 µm), which may subsequently be inhaled. Inhalation of zinc oxide particles and fumes by workers can result in metal fume fever (Martin et al. 1999). Inhalation was reported to be the most probable route of exposure to zinc for 26 lead smelter workers found to have significantly (p<0.01) elevated blood plasma levels of zinc. Mean plasma zinc concentrations were 12.9 mmol/L (range, 9.8–16.7) for the workers versus 10.9 mmol/L (range, 8.1–14.6) for a nonlead-exposed control group (Vasikaran et al. 1992). Twenty workers in a zinc foundry in Baiyin, China were investigated for exposure to zinc oxide fumes (Martin et al. 1999). Eighteen of the workers had worked at the foundry since its opening 6 years earlier. Thirteen of the subjects reported at least one of the symptoms associated with metal fume fever during their tenure at the foundry. Workers were examined before the start of the

shift, in the middle of the shift, and after the shift. Despite zinc exposures as high as 36.3 mg/m^3 over <4 hours and a mean air sample concentration of 3.16 mg/m^3, no cases of metal fume fever were observed for these workers. Concentrations of zinc in serum and urine for these workers averaged 11.515 µmol/L (752.85 µg/L) and 3.6705 µmol/L (239.98 µg/L), respectively, during the period of an 8-hour shift.

Zinc is found in human tissues and body fluids. As part of the 1982 National Human Adipose Tissue Survey (NHATS) conducted in the United States, the concentration of zinc in adipose tissue ranged from 1.1 to 6.0 µg/g (EPA 1986). The mean concentration of zinc was 6.95±1.08 µg/mL in whole blood samples from residents of Baajoz, Spain (a region with low environmental pollution) with zinc levels increasing with age (Moreno et al. 1999). Individuals <30, 30–45, and >45 years old had whole blood zinc concentrations of 4.85, 6.85, and 7.32 µg/mL, respectively. Blood and serum collected from 372 adolescents (15 years old) from the Swedish cities of Uppsala and Trollhättan contained zinc at median concentrations of 6.1 and 0.99 mg/L, respectively (Bárány et al. 2002). The mean concentration of zinc in the fingernails and toenails of populations from the United States, Canada, and Japan were 105, 109, and 94 mg/kg, respectively (Takagi et al. 1988). Hayashi et al. (1993) reported that human fingernail samples from Japanese individuals had higher mean levels of zinc in the spring (145–149 µg/g) compared to winter (122–136 µg/g). The geometric mean concentrations of zinc in toenails (129 mg/kg) and scalp hair (108 mg/kg) of pre-school children in Germany were about the same (Wilhelm et al. 1991). The total concentrations of zinc in 29 body tissues of 55 human cadavers were measured (Saltzman et al. 1990). The lowest concentration (mean of 1.5±2.2 mg/kg wet weight) of zinc in both males and females was found in adipose tissues, while the highest concentrations were detected in the skull of males (mean of 54.3 mg/kg wet weight) and in the skeletal muscle of females (mean of 59.0 mg/kg wet weight). The mean concentrations of zinc in the feces of low-income urban Hispanics and rural Blacks in the United States were 75 and 94 mg/kg wet weight, respectively (Prevost et al. 1985). Body tissue and fluid samples were collected from two nonoccupationally exposed individuals living in the Los Angeles, California area (Krishnan and Que Hee 1992). Ear wax, blood plasma, sweat, and skin from these individuals contained zinc at levels of 88–103, 0.79–1.7, 0.50–1.58, and 15.6–1,000 µg/g dry weight, respectively.

Concentrations of zinc in human milk are affected by the stages lactation. Arnaud and Favier (1995) found that the level of zinc in human milk will rise to a peak 2-days postpartum (183±70 µmol/L or 12.0±4 mg/L) and then decline during the duration of lactation (e.g., at 6-days postpartum, 77±22 µmol/L or 5.0±1.4 mg/L). At 6-months, the concentration of zinc in human milk is only 12% of its initial levels (Dórea 2002). Wasowicz et al. (2001) observed an inverse relationship between zinc levels in blood

plasma and human milk for lactating women from Poland. Mean levels of zinc in blood plasma increased from 0.51±0.13 mg/L (0–4 days postpartum) to 0.76±0.20 mg/L (10–30 days postpartum), while mean levels of zinc in human milk decreased from 8.2±2.8 mg/L (0–4 days postpartum) to 1.4±0.7 mg/L (10–30 days postpartum).

Zinc levels in maternal blood are normally higher than levels in cord blood. Maternal and cord blood of 56 mothers living in Singapore were analyzed for zinc (Ong et al. 1993). For these mothers, the mean concentrations of zinc were 4.97±1.15 and 1.58±0.45 mg/L in maternal and cord blood, respectively. During the period of 1993–1997, Raghunath et al. (2000) determined the concentration of zinc in maternal and cord blood for 148 mothers (20–25 years old) living Mumbai City, India. The mean concentrations of zinc were 6.335 and 2.527 mg/L in maternal and cord blood, respectively.

Occupational. As part of the National Occupational Exposure Survey (NOES) conducted from 1980 to 1983, NIOSH statistically estimated that 269 workers (including 22 women) in 22 plants were potentially exposed to elemental zinc in the workplace; also, 133,608 workers (including 17,586 women) in 6,157 plants were potentially exposed to other forms of zinc (of undefined composition) in the workplace (NIOSH 1984b). All of the workers exposed to elemental zinc were employed in the fabricated metal products industry as millwrights or assemblers. The largest numbers of workers exposed to other forms of zinc worked in the primary metal industries, with fabricated metal products, with transportation equipment, with stone, clay, and glass products, and in special trade contractors industries. Occupational groups with the largest numbers of exposed workers were miscellaneous machine operators (not elsewhere classified or not specified), molding and casting machine operators, janitors and cleaners, and machinists. Exposure estimates were derived from observations of the actual use of the compound and the use of trade name products known to contain the compound.

6.6   EXPOSURES OF CHILDREN

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

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk

or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

As for adults, sources of exposure for children to zinc include ingestion of food, drinking water, and polluted air, with ingestion of food being the primary route of exposure. In an extensive survey of foods in the total diets of children in the United States, conducted by FDA during 1982–1984, the following values for daily zinc intakes (mg/day) were estimated: 6–11-month-old infants, 5.24; 2-year-old children, 7.37; 14–16-year-old girls, 9.90; and 14–16-year-old boys, 15.61 (Pennington et al. 1986). The FDA also included drinking water in the total diet. Hair samples collected from children (10–12 years old) living rural and industrial areas of southern Poland and analyzed for zinc (Zachwieja et al. 1995). Hair samples of children from Kraków-Shakina (urban areas), Tarnów-Czechowice-Dziedzice (industrial areas), and rural areas contained zinc at concentrations of 171.5, 185.0, and 244.6 ppm, respectively (Zachwieja et al. 1995). Whole blood samples from children (3–6 years old) living in Mumbai and Hyderabad, industrialized urban areas of India, contained zinc at mean concentrations of 398.9 and 483.4 µg/dL, respectively (Tripathi et al. 2001).

At waste sites, zinc that is found in excess of natural background levels is most likely to be in soil, and presents a special hazard for young children. Hand-to-mouth activity and eating contaminated dirt will result in oral exposure to zinc. The hazard in this case depends on the form of zinc that is present at the waste site. Zinc in soil at waste sites is in both soluble and insoluble forms; zinc in insoluble forms would be expected to be less available than more soluble forms.

Zinc exposure to children from parents' work clothes, skin, hair, tools, or other objects from the workplace is possible if the parent uses zinc or its compounds at work. Household products or products used in crafts, hobbies, or cottage industries which contain galvanized materials (e.g., nails) or zinc-containing paint will have significant amounts of zinc. Hand-to-mouth activity, chewing, and eating these materials may result in higher exposure to zinc. However, no cases of home exposure to zinc were located in the literature.

6.7   POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Certain populations receive greater-than-average exposures to zinc from environmental sources. For example, higher levels of zinc have been reported in soil and water near waste sites, metal smelters, and areas exposed to untreated waste water (Hutchinson and Wai 1979; Ragaini et al. 1977; Schalscha et al. 1982). Other populations at risk of high exposure are those that have galvanized plumbing in their residences, and those that intentionally consume large doses of zinc as a dietary supplement. Patients who receive chronic treatment with drugs containing zinc salts (such as injectable insulin) are exposed to higher zinc levels than the general population. Allergic reactions to the zinc in insulin have been reported (Bruni et al. 1986). People in certain occupations (e.g., nonferrous metal smelting) are likely to be exposed to higher concentrations of zinc than the general population (see Section 6.5). However, the higher exposure may not be indicative of a long-term increase in body burden. For example, the median zinc concentration in the lung tissues of 21 Swedish workers previously employed in the refining and smelting of nonferrous metals was about the same as in a control group (11.0 versus 10.7 mg/kg wet weight) (Hewitt 1988). On the other hand, the median concentration of zinc in lung tissues of eight deceased coal miners from England was 72 mg/kg wet weight compared to a median value of 54 mg/kg wet weight for a control group (Hewitt 1988); however, the study author did not provide any evidence that the difference in zinc concentrations in the lungs of unexposed controls is statistically significant.

Individuals who smoke or who use zinc supplementation will have greater exposure to zinc. Zinc was measured in samples of cigarette tobacco from the United States at concentrations ranging from 30 to 69 µg/g (Jenkins 1986). Levels of zinc in smoke from these cigarettes ranged from 0.34 to 1.21 µg/cigarette. Individuals, who use high-dose zinc supplementation as a potential treatment for age-related macular degeneration, will have higher exposures to zinc. Hiller et al. (1995) reported that zinc supplements will have an effect on the concentration of serum zinc in the body.

6.8   ADEQUACY OF THE DATABASE

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

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

6.8.1   Identification of Data Needs

Physical and Chemical Properties.   Data are available that adequately characterize the physical and chemical properties of the various forms of zinc to permit estimation of their environmental fate (ACGIH 1991; Baes and Sharp 1983; Baes et al. 1984; Gerritse et al. 1982; HSDB 1986, 1990; NIOSH 1990; Weast 1988; Weiss 1986; Windholz 1983).

Production, Import/Export, Use, Release, and Disposal.   According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information for 2002, became available in May of 2004. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Information about current and future production of zinc and zinc compounds is available. Zinc is also one of the most widely used metals in the world (Mirenda 1986). In 2001, approximately 799,000 metric tons of zinc were produced in the United States from domestic ores. The estimated world production from mines in 2001 was 8,850,000 metric tons (USGS 2001). Information on the use of zinc and its compounds in the home, environment, and workplace is available. Zinc is most commonly used as a protective coating for other metals. It is also used in alloys such as bronze and brass, for electrical apparatus, and in organic chemical extractions. Zinc salts have numerous applications, including wood preservation. Zinc chloride is a primary ingredient in smoke bombs. In pharmaceuticals, zinc salts are used as solubilizing agents in drugs, including insulin (Lloyd 1984; Lloyd and Showak 1984; Windholz 1983). Zinc oxide is found in ointments used to treat burns and infectious and skin diseases (EPA 1987d). Zinc is also utilized therapeutically in human medicine in the treatment of zinc deficiency (Elinder 1986). Information on typical releases of zinc and its compounds in the home, environment, and workplace, and which environmental media are likely to be contaminated with significant quantities of zinc are available. Zinc is ubiquitous in the environment. Both natural releases and releases of human

origin to the environment can be significant (EPA 1980d; Fishbein 1981; Mirenda 1986; NAS 1977; Nriagu 1989; Ragaini et al. 1977; TRI02 2004). Soils and sediments are likely to contain significant quantities of zinc and its compounds (Connor and Shacklette 1975; Rice 1999; Shacklette and Boerngen 1984; USGS 2002). Current disposal methods are efficient (Dawson and Mercer 1986; Lloyd and Showak 1984). No data were located regarding the amount of zinc being disposed. Rules and regulations regarding the disposal of zinc are available (Dawson and Mercer 1986; DOI 1991). According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to EPA. The Toxics Release Inventory (TRI) contains this information for 2001. Environmental releases of zinc and zinc compounds from manufacturing and processing facilities required to report their releases are listed in Tables 6-1 and 6-2. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate.   Zinc partitions to the air, water, and soil (EPA 1979d; Guy and Chakrabarti 1976; Houba et al. 1983; Pita and Hyne 1975). Zinc occurs in the environment mainly in the +2 oxidation state (Lindsey 1979). Adsorption is the dominant fate of zinc, resulting in enrichment of zinc in suspended and bed sediments (EPA 1979d). The mobility of zinc in soil has been characterized (Baes and Sharp 1983; Bergkvist et al. 1989; EPA 1980d; Hermann and Neumann-Mahlkau 1985; Kalbasi et al. 1978; Saeed and Fox 1977; Tyler and McBride 1982). No estimate for the atmospheric lifetime of zinc is available. Development of pertinent data on the atmospheric processes important for zinc speciation in the atmosphere would be helpful. Development of this information would permit construction of a comprehensive model for the transport and interaction of zinc not only in air but in other media as well. Transformation in air and water can occur as a result of changes in chemical speciation (Anderson et al. 1988; EPA 1979d, 1980d; Stokinger 1981). Data that describe the transformation processes for zinc in soil or the fate of zinc in soil are needed. A model of zinc flux from all environmental compartments would be useful for providing information on the overall environmental fate of zinc.

The primary anthropogenic sources of zinc in the environment (i.e., air, water, soil) are related to mining and metallurgic operations involving zinc and use of commercial products containing zinc (EPA 1980d; NAS 1977; Nriagu and Pacyna 1988; Ragaini et al. 1977; TRI02 2004). Zinc has been detected in air, surface water, groundwater, and soil, with the frequency of detection and the concentrations greatest near source areas (e.g., hazardous waste sites and industrial areas such as lead smelters) (EPA 1980d; HazDat 2005; Lioy et al. 1978; Lloyd and Showak 1984; Mumma et al. 1984, 1990, 1991; NAS 1977).

Bioavailability from Environmental Media.   Zinc can be absorbed following inhalation (Drinker and Drinker 1928; Hamdi 1969), ingestion (Aamodt et al. 1983; Davies 1980; Johnson et al. 1988; Methfessel and Spencer 1973; NAS/NRC 1979; Spencer et al. 1985), or dermal contact (Agren 1990; Gordon et al. 1981; Hallmans 1977; Keen and Hurley 1977). No estimates of the bioavailability of zinc after inhalation of zinc particles in air, ingestion from water and soil, or skin contact with bath water or soil were located. The bioavailability of zinc is higher in media with a low pH, as a result of increased zinc solubility and ionization. If zinc is partly present in an irreversibly adsorbed state in soil, this part is not available for skin absorption. It would be useful to develop quantitative data on the bioavailability of zinc from various environmental media.

Food Chain Bioaccumulation.   Zinc bioconcentrates moderately in aquatic organisms, and this bioconcentration is higher in crustaceans and bivalve species than in fish (EPA 1987c; Ramelow et al. 1989). Zinc may concentrate in plants grown on contaminated soils. However, it does not biomagnify through the terrestrial food chain (Biddinger and Gloss 1984; EPA 1979d; Hegstrom and West 1989; Levine et al. 1989).

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

Zinc has been detected in air (Barrie and Hoff 1985; Duce et al. 1975; EPA 1980d; Evans et al. 1984; John et al. 1973; Lioy et al. 1978; Lloyd and Showak 1984; Patterson et al. 1977; Pratt et al. 2000; Ragaini et al. 1977; Saltzman et al. 1985; Spicer et al. 1996; Zoller et al. 1974), water (Bruce and McMahon 1996; Coale and Flegal 1989; Cole et al. 1984; EPA 1980d; Hale 1977; HazDat 2005; Heit et al. 1989; Maessen et al. 1985; Minear et al. 1981; NAS 1977; Nriagu et al. 1996; Ohanian 1986; Sañudo-Wilhelmy and Gill 1999; Schock and Neff 1988; Scudlark et al. 1994; Shiller and Boyle 1985; Taylor et al. 2001; Windom et al. 1991), soil (Beavington 1975; Chen et al. 1999; Connor and Shacklette 1975; EPA 1980d; Haines 1984; HazDat 2005; Johnson et al. 1990; Mayer and Manning 1990; Mielke et al. 1999, 2000; Mumma et al. 1984, 1990, 1991; Norrström and Jacks 1999; Schalscha et al. 1982; Storm et al. 1994), and food (Coleman et al. 1992; FDA 2001; Gartrell et al. 1986a; Mahaffey et al. 1975; Weigert 1991). However, since most of the data are not current, i.e., within the last 3 years, additional data would be useful to provide a more complete characterization of human exposure and the trend in zinc concentrations in various environmental media. Estimates have been made for human intake of zinc from

food and drinking water (EPA 1980d; Gartrell et al. 1986a; IOM 2002; Pennington et al. 1986; Sharrett et al. 1982a, 1982b). Further data are needed on estimated daily intakes from inhalation resulting from occupational exposures.

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

Exposure Levels in Humans.   Zinc has been detected in fingernails, toenails, hair, all tissues, organs, skull and skeletal muscle, blood, feces, urine, sweat, and saliva (Greger and Sickles 1979; Hambidge et al. 1972; Henkin et al. 1975a; Llobet et al. 1988a; NAS/NRC 1979; Prasad et al. 1963a; Prevost et al. 1985; Saltzman et al. 1990; Schroeder et al. 1967; Takagi et al. 1988; Wastney et al. 1986; Wilhelm et al. 1991). Most of the data on occupational exposure levels of zinc are outdated (NIOSH 1976, 1984b). Additional information on potentially exposed workers and exposure levels would provide a more accurate characterization of occupational exposures in the United States. Current biological monitoring data on zinc are needed for populations surrounding hazardous waste sites. This information is necessary for assessing the need to conduct health studies on these populations.

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

Exposures of Children.   Limited data are available regarding the exposure and body burdens of children to zinc. Children, like adults, are primarily exposed to zinc through the diet. Zinc was identified in the postpartum human milk of women at concentrations of 5 to 12 mg/L (Arnaud and Favier 1995). In an extensive survey of foods in the total diets of individuals in the United States, conducted by FDA during 1982–1984, the following values for daily zinc intakes (mg/day) were estimated for children: 6–11-month-old infants, 5.24; 2-year-old children, 7.37; 14–16-year-old girls, 9.90; and 14–16-year-old boys, 15.61 (Pennington et al. 1986). Since zinc is found in soil and children ingest soil either intentionally through pica or unintentionally through hand-to-mouth activity, pica is a unique exposure pathway for children. While zinc is found in home products such as paint, ointments, galvanized metals, coins, and dietary supplements, this exposure route should be low and will not disproportionally affect children. Continued monitoring data are necessary to understand potentially dangerous routes of childhood exposure.

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

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

6.8.2   Ongoing Studies

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

Table 6-6. Ongoing Studies on the Environmental Effects of Zinc[a]

Investigator	Affiliation	Study	Sponsor
Ahner BA	Cornell University, Biological and Environmental Engineering	Monitoring the bioavailability of toxic metals in soil	USDA
Basta N, Raun WR	Oklahoma State University, Agronomy	Chemistry and bioavailability of waste constituents in soils	USDA
Basta NT	Oklahoma State University, Agronomy	Heavy metal and trace element chemistry in soils: Chemical speciation and bioavailability	USDA
Bleam WF, Helmke PA	University of Wisconsin Soil Science	Verifying and quantifying the specific complexation of metals to humic substances	USDA
Chaney RL	Beltsville Agricultural Research Center	Characterization and remediation of potential trace element and phosphate risks from contaminated soils	USDA
Chaney RL	Beltsville Agricultural Research Center	Development of methods to control heavy metal contents in soils at benign or beneficial levels	USDA
Chaney RL	Beltsville Agricultural Research Center	Long-term phytoavailability and bioavailability of soil metals	USDA
Chaney RL, Angle JS	University of Maryland, Agronomy	Phytoavailability and bioavailability of heavy metals from heavy metal contaminated soil	USDA
Cox FR	North Carolina State University, Soil Science	Effects of P, Cu, and Zn from animal waste and fertilizer on crop responses and soil test interpretations	USDA
Fish RH	Lawrence Berkeley Laboratory, University of California	Removal and recovery of toxic metal ions from aqueous streams by utilization of polymer pendant ligands	DOE
Guo MG, Tyzbir R	University Of Vermont, Nutritional Sciences	Solubility and distribution of trace elements in milk based infant formula	USDA
Harsh JB, Zamora BA, Kuo S, Pan W, Stevens RG, Flury M	Washington State University, Crop and Soil Sciences	Physical chemical state and plant availability of uranium, lead, cadmium, zinc, and arsenic in selected Washington soils	USDA
Heil D	Colorado State University, Soil and Crop Science	Biogeochemistry and management of salts and potentially toxic trace elements in arid-zone soils, sediments, and water	USDA
Helmke PA, Bleam WF	University of Wisconsin Soil Science	Reactions controlling free ion activities and solubility of soil trace elements	USDA
Hesterberg DL	North Carolina State University, Soil Science	Molecular-scale characterization and fate of soil contaminants	USDA
Kinraide TB	Agricultural Research Service	The role of binding and electrostatic attraction to roots in the uptake of heavy metals by plants	USDA
Kochian LV, Paolillo DJ	Cornell University, Plant Biology	Mechanisms of aluminum tolerance and heavy metal accumulation in plants	USDA

Table 6-6. Ongoing Studies on the Environmental Effects of Zinc[a]

Investigator	Affiliation	Study	Sponsor
Kochian LV	Agricultural Research Service	Investigation of heavy metal bioaccumulation in plants grown on metal-polluted soils	USDA
Kochian LV	Agricultural Research Service	Mechanisms of heavy metal and radionuclide hyper-accumulation and bioavailability in higher plants	USDA
Kpomblekou-Ademawou K, Ankumah RO	Tuskegee University, Agriculture and Home Economics	Trace elements in broiler littered soils: fate and effects on nitrogen transformation	USDA
Kuo S	Washington State University, Puyallup Research and Extension Center	Chemistry and bioavailability of waste constituents in soils	USDA
Little RE	NIEHS, National Institutes of Health	Environmental pollution in eastern and central Europe	NIH
McBride MB	Cornell University, Soil, Crop and Atmospheric Science	Heavy metal solubility in contaminated soils	USDA
McBride MB	Cornell University, Soil, Crop and Atmospheric Science	Reaction and availability of toxic metals in soils	USDA
Norvell WA, Duxbury JM	Cornell University	Plant availability and geographical distribution of essential and toxic elements	USDA
Norvell WA, Welch RM, Degloria SD	Cornell University	Bioavailability and geographic distribution of nutritionally important elements in crops and soils	USDA
Odom JW	Auburn University, Agronomy and Soils	Occurrence, measurement and mapping of plant micronutrient and trace elements in Alabama soils	USDA
Parker DR	University of California, Environmental Sciences	Predicting trace-metal bioavailability from soil solution speciation: can it be done	USDA
Pierzynski GM	Kansas State University, Agronomy	Chemistry and bioavailability of waste constituents in soils	USDA
Ross DS	University of Vermont, Plant and Soil Science	Soil manganese oxides: Oxidation and retention of contaminant metals and organics	USDA
Salt DE	Purdue University, Horticulture	A dissection of the molecular mechanisms underlying metal hyperaccumulation in plants	USDA
Slaton NA	University of Arkansas, Crop, Soil and Environmental Sciences	Evaluation of fertilization practices, soil fertility, and plant nutrition for crops produced in Arkansas	USDA
Sparks DL, Ford RG	University of Delaware, Plant and Soil Sciences	Influence of aging and competitive sorption on stabilization of metals via surface precipitation in soils	USDA
Thompson ML	Iowa State University, Agronomy	Co-migration of metals and dissolved humic substances in aquifer material	USDA

Table 6-6. Ongoing Studies on the Environmental Effects of Zinc[a]

Investigator	Affiliation	Study	Sponsor
Thompson ML	Iowa State University, Agronomy	Sustainable and environmentally safe management of soil resources	USDA
Welch RM, Norvell WA, Kochian LV	Agricultural Research Service	Agricultural approaches to human health through understanding soil-plant-human/animal food systems	USDA
Zelazny LW	Virginia Polytechnic Institute, Crop and Soil Environmental Sciences	Soil mineralogical controls on nutrient availability and mobility	USDA

[a]Source: FEDRIP 2004

DOE = Department of Energy; FEDRIP = Federal Research in Progress Database; NIEHS = National Institute of Environmental Health Services; NIH = National Institute of Health; USDA = United Stated Department of Agriculture