

## 6. POTENTIAL FOR HUMAN EXPOSURE

### 6.1 OVERVIEW

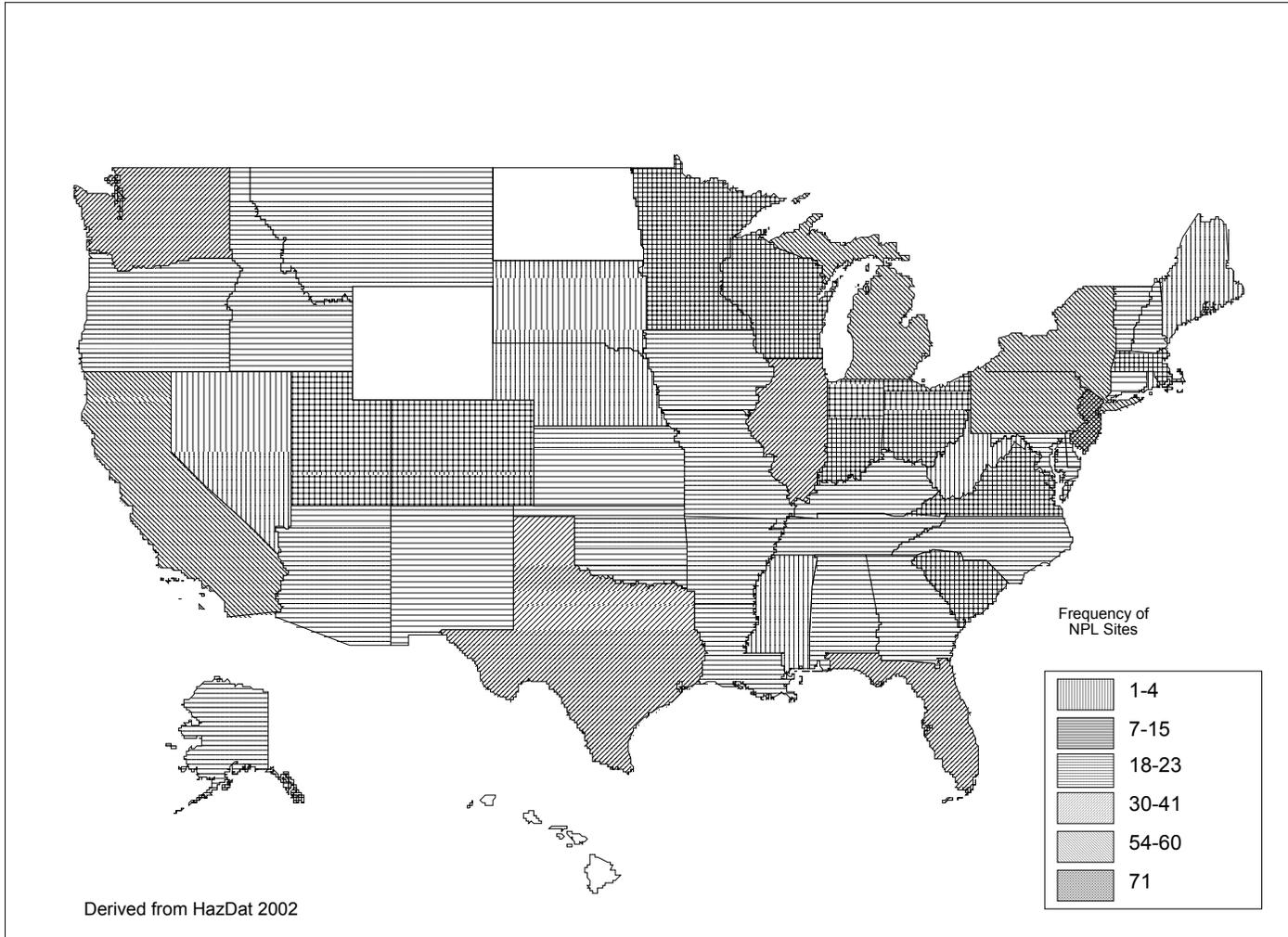
Copper has been identified in at least 884 of the 1,613 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2002). However, the number of sites evaluated for copper is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, 873 are located within the United States, 8 are located in the Commonwealth of Puerto Rico, 1 is located in the Virgin Islands, and 2 are located in the Territory of Guam (the Commonwealth of Puerto Rico, the Virgin Islands, and the Territory of Guam are not shown in Figure 6-1).

Copper and its compounds are naturally present in the earth's crust. Natural discharges to air and water, such as windblown dust, volcanic eruptions, etc., may be significant. Therefore, it is important to consider the background levels that are commonly found in order to distinguish these from levels that can be attributed to anthropogenic activity.

The median concentration of copper in natural water is 4–10 ppb. It is predominantly in the Cu(II) state. Most of it is complexed or tightly bound to organic matter; little is present in the free (hydrated) or readily exchangeable form. The combined processes of complexation, adsorption, and precipitation control the level of free Cu(II). The chemical conditions in most natural water are such that, even at relatively high copper concentrations, these processes will reduce the free Cu(II) concentration to extremely low values. Sediment is an important sink and reservoir for copper. In relatively clean sediment, the copper concentration is <50 ppm; polluted sediment may contain several thousand ppm of copper. The form of copper in the sediment will also be site-specific. Organics (humic substances) and iron oxides are the most important contributor to binding of copper by aerobic sediments. However, in some cases, copper is predominantly associated with carbonates. In anaerobic sediment, Cu(II) will be reduced to Cu(I) and insoluble cuprous salts will be formed.

The largest release of copper by far will be to land, and the major sources of release are mining operations, agriculture, solid waste, and sludge from publicly-owned treatment works (POTWs). Mining and milling contribute the most waste.

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



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Copper is released to water as a result of natural weathering of soil and discharges from industries and sewage treatment plants. Most of this copper is attached to particulate matter. Copper compounds may also be intentionally applied to water to kill algae. Of special concern is copper that gets into drinking water from the water distribution system. When the system has not been flushed after a period of disuse, the concentration of copper in tap water may exceed 1.3 ppm, the EPA drinking water limit.

Copper is emitted into the air naturally from windblown dust, volcanoes, and anthropogenic sources, the largest of which are being primary copper smelters and ore processing facilities. It is associated with particulate matter. The mean concentration of copper in the atmosphere is 5–200 ng/m<sup>3</sup>. In comparison, the concentration of copper in emissions from copper smelters have been found to range between 7 and 137.8 ng/m<sup>3</sup> (Hutchinson 1979; Romo-Kröger et al. 1994).

The general population may be exposed to high concentrations of copper from drinking water that has picked up copper from the distribution system (both from the water treatment plant and in the home). Contact with available copper may also result from using copper fungicides and algicides. Many workers are exposed to copper in agriculture, industries connected with copper production, metal plating, and other industries. Little information is available concerning the forms of copper to which workers are exposed. At this time, copper has been identified at 873 out of 1,613 NPL hazardous waste sites in the United States (HazDat 2002). The frequency of these sites within the United States can be seen in Figure 6-1. While experiments show that copper does not leach significantly from soil, levels of copper as high as 2.8 ppm have been found in some groundwater (Page 1981).

## 6.2 RELEASES TO THE ENVIRONMENT

Industrial manufacturers, processors, and users of copper and copper compounds are required to report the quantities of this substance released to environmental media annually (EPA 1988d). The data compiled in the Toxics Release Inventory (TRI00 2002), are for releases in 2000 to air, water, soil, and transfers for offsite disposal. These data are summarized in Tables 6-1 (copper) and 6-2 (copper compounds). Total releases (rounded to three-place accuracy) of copper into the environment in 2000 were approximately 9,210,000 pounds (approximately 4,180 metric tons) (TRI00 2002), of which approximately 1,180,000 pounds (536 metric tons), or 12.8% of the total, were released to air. Another 40,000 pounds (18 metric tons) or approximately 0.4% of the total, were released into water, 0.8% (70,600 pounds, 32 metric tons) was injected underground, and 86.0% (7,920,000 pounds, 3,600 metric

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

State <sup>b</sup>	Number of facilities	Reported amounts released in pounds per year <sup>a</sup>						Total on and off-site release
		Air <sup>c</sup>	Water	Underground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	
AL	45	15,983	1,820	No data	454	18,257	348,725	366,982
AR	44	5,932	1,727	No data	186,925	194,584	333,088	527,672
AZ	27	1,812	537	No data	81,842	84,191	41,647	125,838
CA	153	35,838	1,320	No data	309,783	346,941	57,669	404,611
CO	15	1,097	21	No data	55,556	56,674	25,937	82,611
CT	50	12,357	1,646	No data	1,503	15,506	106,385	121,891
DE	1	No data	No data	No data	No data	No data	No data	0
FL	20	2,381	1,455	67,858	631	72,325	56,440	128,765
GA	48	3,498	807	No data	31,670	35,975	389,388	425,363
IA	32	3,623	261	No data	4,603	8,487	127,744	136,231
ID	4	297	No data	No data	544,000	544,297	5,780	550,077
IL	151	63,734	5,537	No data	1,645,215	1,714,486	845,173	2,559,659
IN	158	51,990	1,417	No data	147,739	201,146	2,421,974	2,623,120
KS	26	5,890	251	No data	63,005	69,146	61,547	130,693
KY	69	25,029	485	No data	62,455	87,969	245,453	333,422
LA	7	22	738	2,100	205	3,065	15,927	18,992
MA	63	5,338	68	No data	No data	5,406	78,600	84,006
MD	7	253	10	No data	250	513	85,596	86,109
ME	9	114	31	No data	5	150	9,139	9,289
MI	130	115,647	670	17	167	116,501	616,441	732,942
MN	49	20,778	8	No data	5	20,791	939,660	960,451
MO	77	22,823	612	No data	9,826	33,261	178,639	211,900
MS	29	2,685	129	No data	505	3,319	66,681	70,000
MT	2	417	No data	No data	2,940,000	2,940,417	No data	2,940,417
NC	67	8,575	1,563	0	272	10,410	1,471,083	1,481,493

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Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Copper (continued)

State <sup>b</sup>	Number of facilities	Reported amounts released in pounds per year <sup>a</sup>						Total on and off-site release
		Air <sup>c</sup>	Water	Underground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	
ND	2	18	15	No data	No data	33	707	740
NE	19	4,185	31	No data	36,000	40,216	14,260	54,476
NH	20	1,057	25	No data	0	1,082	141,099	142,181
NJ	40	19,383	171	1	No data	19,555	11,202	30,757
NM	6	500	No data	No data	48,117	48,617	27,837	76,454
NV	5	502	No data	No data	21,000	21,502	93	21,595
NY	91	15,456	3,752	No data	63	19,271	643,566	662,837
OH	223	49,464	6,083	0	1,180,213	1,235,760	635,915	1,871,675
OK	46	15,142	307	No data	52,882	68,331	69,013	137,344
OR	18	784	6	No data	14,754	15,544	1,765	17,309
PA	215	107,564	2,668	No data	45,649	155,881	2,504,799	2,660,680
PR	22	15,251	35	No data	5	15,291	1,155	16,446
RI	29	6,569	5	No data	0	6,574	39,076	45,650
SC	51	13,643	685	No data	4,425	18,753	185,338	204,091
SD	8	19	No data	No data	No data	19	10,818	10,837
TN	87	421,476	868	No data	461	422,805	316,473	739,278
TX	95	18,694	1,187	596	155,144	175,621	251,209	426,830
UT	10	192	17	No data	10,767	10,976	40,103	51,079
VA	44	39,599	1,095	No data	160,092	200,786	157,407	358,193
VT	3	No data	No data	No data	250	250	760	1,010
WA	28	1,987	695	No data	12,463	15,145	87,031	102,176
WI	126	39,480	873	No data	2,058	42,411	427,058	469,469

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**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Copper (continued)**

State <sup>b</sup>	Number of facilities	Reported amounts released in pounds per year <sup>a</sup>						Total on and off-site release
		Air <sup>c</sup>	Water	Underground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	
WV	14	1,951	27	5	30,158	32,141	35,481	67,622
WY	3	392	1	No data	57,046	57,439	93	57,532
Total	2,487	1,179,421	39,659	70,577	7,918,163	9,207,819	14,130,974	23,338,793

Source: TRI00 2002

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

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

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

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

<sup>e</sup>Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

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

State <sup>b</sup>	Number of facilities	Reported amounts released in pounds per year <sup>a</sup>						Total on and off-site release
		Air <sup>c</sup>	Water	Underground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	
AK	4	470	38	1,300,000	4,856,411	6,156,919	750	6,157,669
AL	39	25,437	21,433	No data	12,406,258	12,453,128	183,324	12,636,452
AR	25	16,170	4,726	No data	110,712	131,608	481,062	612,670
AZ	28	183,722	1,796	No data	579,148,733	579,334,251	330,839	579,665,090
CA	79	6,130	734	No data	1,166,647	1,173,511	482,758	1,656,269
CO	8	752	11,808	No data	106,817	119,377	77,684	197,061
CT	22	2,626	797	No data	0	3,423	195,677	199,100
DC	2	No data	3	No data	3,017	3,020	No data	3,020
DE	4	2,113	9,700	No data	25,546	37,359	27,738	65,097
FL	34	83,333	21,193	42	1,024,922	1,129,490	151,922	1,281,412
GA	27	20,006	51,039	No data	839,269	910,314	1,716,060	2,626,374
IA	25	24,248	2,922	No data	170,605	197,775	115,212	312,987
ID	7	1,288	230	No data	706,894	708,412	20,616	729,028
IL	94	46,302	4,294	No data	541,813	592,409	986,870	1,579,279
IN	72	88,214	17,573	1,300	1,102,587	1,209,674	1,248,657	2,458,331
KS	9	4,026	255	No data	166,107	170,388	69,525	239,913
KY	40	34,176	30,153	No data	853,002	917,331	440,093	1,357,424
LA	21	6,380	18,145	No data	163,296	187,821	264,589	452,410
MA	24	872	30	No data	1,400	2,302	91,024	93,326
MD	8	1,232	7,056	No data	16,700	24,988	14,057	39,045
ME	5	2,200	0	No data	0	2,200	43,484	45,684
MI	55	95,317	10,004	No data	551,990	657,311	561,607	1,218,918
MN	28	9,668	971	No data	327,020	337,659	1,600,338	1,937,997
MO	35	38,164	3,229	No data	4,909,325	4,950,718	358,332	5,309,050

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**Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Copper Compounds  
(continued)**

State <sup>b</sup>	Number of facilities	Reported amounts released in pounds per year <sup>a</sup>						Total on and off-site release
		Air <sup>c</sup>	Water	Underground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	
MS	12	34,588	1,044	21,000	64,900	121,532	156,630	278,162
MT	9	12,936	9	No data	15,557,393	15,570,338	135,358	15,705,696
NC	50	26,734	43,507	No data	747,663	817,904	133,282	951,186
ND	7	654	10,862	No data	126,430	137,946	168,818	306,764
NE	9	6,482	339	No data	279,658	286,479	404,286	690,765
NH	10	775	21	No data	500	1,296	36,763	38,059
NJ	27	2,148	10,065	No data	26,186	38,399	407,668	446,067
NM	6	16,449	5,305	No data	83,263,458	83,285,212	178,260	83,463,472
NV	18	325,559	310	11	32,068,686	32,394,566	173,849	32,568,415
NY	31	14,128	11,379	No data	1,005,441	1,030,948	614,160	1,645,108
OH	82	18,867	31,896	190,000	1,305,202	1,545,965	1,281,479	2,827,444
OK	16	2,918	6,838	675	356,902	367,333	85,090	452,423
OR	14	2,737	1,339	No data	156,061	160,137	126,215	286,352
PA	92	145,905	4,798	0	459,070	609,773	3,625,910	4,235,683
PR	3	300	550	0	0	850	23,760	24,610
RI	10	15	61	No data	No data	76	15,244	15,320
SC	36	42,578	6,926	No data	261,695	311,199	599,382	910,581
SD	2	412	No data	No data	22,000	22,412	951	23,363
TN	46	20,870	24,684	0	1,682,648	1,728,202	252,578	1,980,780
TX	93	87,395	12,737	224,223	1,499,493	1,823,848	1,696,719	3,520,567
UT	14	127,695	1,010	No data	596,061,674	596,190,379	193,222	596,383,601
VA	38	44,688	9,886	No data	383,479	438,053	242,073	680,126
WA	18	13,972	1,075	No data	203,260	218,307	97,606	315,913
WI	43	7,755	11,422	No data	19,654	38,831	260,785	299,616

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**Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Copper Compounds  
(continued)**

State <sup>b</sup>	Number of facilities	Reported amounts released in pounds per year <sup>a</sup>						Total on and off-site release
		Air <sup>c</sup>	Water	Underground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	
WV	17	4,990	12,140	0	1,045,151	1,062,281	159,356	1,221,637
WY	4	1,710	87	No data	266,170	267,967	43,000	310,967
Total	1,402	1,656,106	426,419	1,737,251	1,346,061,845	1,349,881,621	20,574,661	1,370,456,283

Source: TRI00 2002

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

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

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

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

<sup>e</sup>Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

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tons) was released to land. Total releases (rounded to three-place accuracy) of copper compounds to the environment in 2000 were approximately 1,350,000,000 pounds (approximately 613,000 metric tons) (TRI00 2002), of which approximately 1,660,000 pounds (752 metric tons), or 0.1% of the total, were released to air. Another 426,000 pounds (194 metric tons) or approximately 0.03% of the total, were released into water, 0.1% (1,740,000 pounds, 789 metric tons) was injected underground, and 99.7% (1,350,000,000 pounds, 611,000 metric tons) was released to land. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Industrial releases are only a fraction of the total environmental releases of copper and copper compounds. Other sources of copper release into the environment originate from domestic waste water, combustion processes, wood production, phosphate fertilizer production, and natural sources (e.g., wind blown dust, volcanoes, decaying vegetation, forest fires, and sea spray) (Georgopoulos et al. 2001). Quantitative information on release of copper to specific environmental media are discussed below; a summary of copper concentrations in environmental media is provided in Table 6-3.

### 6.2.1 Air

Copper is emitted into the air from both natural and anthropogenic sources. Since copper is a component of the earth's crust, the primary natural source of copper is windblown dust with an estimated mean worldwide emission of  $0.9\text{--}15 \times 10^6$  kg/year (WHO 1998). Other natural sources of copper emitted into air, including estimated mean worldwide emissions, are forest fires ( $0.1\text{--}7.5 \times 10^6$  kg/year), volcanoes ( $0.9\text{--}18 \times 10^6$  kg/year), biogenic processes ( $0.1\text{--}6.4 \times 10^6$  kg/year), and sea spray ( $0.2\text{--}6.9 \times 10^6$  kg/year) (WHO 1998). Anthropogenic emission sources include nonferrous metal production, wood production, iron and steel production, waste incineration, industrial applications, coal combustion, nonferrous metal mining, oil and gasoline combustion, and phosphate fertilizer manufacture. It is estimated that only 0.04% of copper released to the environment is to air (Perwak et al. 1980). Global atmospheric anthropogenic and natural emission of copper have been estimated to be  $35 \times 10^6$  and  $28 \times 10^6$  kg/year, respectively (Guisti et al. 1993).

The EPA conducted a detailed study of copper emissions into the atmosphere to estimate exposure (Weant 1985). The sources of emissions and the estimated quantities of copper emitted in  $10^3$  kg/year are: primary copper smelters, 43–6,000; copper and iron ore processing, 480–660; iron and steel production, 112–240; combustion sources, 45–360; municipal incinerators, 3.3–270; secondary copper

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**Table 6-3. Summary of Copper Concentrations in Environmental Media<sup>a</sup>**

Environmental media		Concentration	Units
Atmosphere			
	Aerosol	0.1–382	ppt
Hydrosphere—water			
Coastal	Dissolved	0.06–4.3	ppb
	Total	0.5–13.8	ppb
	Suspended solids	0.6–370,000	ppm
Estuarine	Dissolved	0.02–4.7	ppb
	Total	1.2–71.6	ppb
	Suspended solids	0.38–72	ppm
Ocean	Dissolved	Not detected–10	ppb
	Total	0.04–10	ppb
	Suspended solids	0.01–2.8	ppm
Lake	Dissolved	0.1–15.6	ppb
	Total	0.1–15.6	ppb
River	Dissolved	0.18–3,000	ppb
	Total	0.5–5,800	ppb
Groundwater	Dissolved	0.003–70	ppb
	Total	1–1,160	ppb
Drinking water	Total	0.3–1,352	ppb
Hydrosphere—sediments			
Coastal	Particulate	0.03–3,789	ppm
	Interstitial water	25.5–32.7	ppb
Estuarine	Particulate	0.3–2,985	ppm
	Interstitial water	0.3–100	ppb
Ocean	Particulate	3.1–648	ppb
	Interstitial water	22–45	ppm
Lake	Particulate	0.4–796	ppm
	Interstitial water	45.6–52	ppb
River	Particulate	5.3–4,570	ppm
Pedosphere			
Soil	Total	0.01–3,138	ppm
	Organic	293–7,634	ppm
Dust	Total	2.9–76	ppm

<sup>a</sup>As reported in the Copper Sourcebook 1998 (Harrison 1998), covering years 1993–1996.

Source: Georgopoulos et al. (2001)

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smelters, 160; copper sulfate production, 45; gray iron foundries, 7.9; primary lead smelting, 5.5–65; primary zinc smelting, 24–340; ferroalloy production, 1.9–3.2; brass and bronze production, 1.8–36; and carbon black production, 13. Using the most probable emission value for primary copper smelters and the range for other sources, estimated U.S. copper emissions are 2,959,000–4,300,000 kg annually. Daily stack emission rates have been reported for three coal-burning power plants on a kg/day/1,000 megawatt basis (Quee Hee et al. 1982); they are 0.3–0.7 and 2.00 kg/day/1,000 megawatt for those using low-sulfur western coal and high-sulfur eastern coal, respectively. In another report, emission of copper into air from a 650 megawatt electrical power plant, burning bituminous coal, was estimated at 213 kg/year, based on a summary of reportable TRI releases (Rubin 1999).

Emission factors in grams of copper released to the atmosphere per ton of product have been estimated for various industries (Nriagu and Pacyna 1988). These factors would enable estimation of an industry's copper emissions from its production volume. Missing from these emission estimates is fugitive dust arising from drilling, blasting, loading, and transporting operations associated with copper mining. The only control of fugitive dust is the manual use of water sprays (EPA 1980b). The highest concentrations of copper in particulate matter were obtained from mining activities, primary and secondary production, and industrial manufacturing (Table 6-4).

Romo-Kröger et al. (1994) were able to show, through the use of radioactive tracers and cluster analysis of interelemental correlations, that Cu, S, Zn, and As measured near a copper smelter in Chile were derived from the plant and not from the surrounding soil. The concentration of copper in air near the plant decreased from 66 ng/m<sup>3</sup> (fine particles) and 131 ng/m<sup>3</sup> (coarse particles) to 22 ng/m<sup>3</sup> (fine particles) and 50 ng/m<sup>3</sup> (coarse particles) during a period of inactivity at the plant, clearly demonstrating the contribution of plant emissions to copper levels in the surrounding area.

The amount of copper and other pollutants originating from copper production sites, such as fugitive dust from smelter bag houses, or waste sites in windblown dust is of some concern. In one study, the amount of airborne copper and other heavy metals deposited near a large refuse dump that received municipal and industrial waste and sewage sludge was determined by first measuring the amount of the metal accumulated in moss bags. The deposition rate was then determined and compared with that for an agricultural control area. The mean copper deposition rates in the two areas were about the same; the maximum deposition rate was twice as much near the dump as in the control area (Lodeni and Braunschweiler 1986).

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**Table 6-4. Concentrations of Copper in Particulate Matter (<10 µm) Generated from Various Sources<sup>a</sup>**

Source	Copper concentration (percent, w/w)
Metal mining	6.17 <sup>b</sup>
Secondary metal production	4.6 <sup>b</sup>
Primary metal production	3.50 <sup>b</sup>
Industrial manufacturing	2.16 <sup>b</sup>
Steel production	0.55 <sup>b</sup>
Gray iron foundries	0.19 <sup>b</sup>
Steel foundry, general	0.17 <sup>b</sup>
Solid waste	0.09 <sup>b</sup>
Food and agriculture	0.05 <sup>b</sup>
Chemical manufacturing	0.03 <sup>b</sup>
Petroleum industry	0.03 <sup>b</sup>
Gasoline vehicle exhaust	0.05 <sup>c</sup>
Paved road dust	0.0162 <sup>c</sup>
Construction dust	0.0102 <sup>c</sup>
Landfill dust	0.0102 <sup>c</sup>
Unpaved road dust	0.0087 <sup>c</sup>
Agricultural lands, dust	0.0067 <sup>c</sup>
Diesel vehicle exhaust	0.003 <sup>c</sup>

<sup>a</sup>Values obtained from CEIDARS 2000

<sup>b</sup>Data obtained from USEPA Speciate 3.0; Shareef, G.S; Radian, September, 1987

<sup>c</sup>Data obtained from KVB Literature Search

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Automobile exhaust has been shown to make small local contributions to copper in air. The amount of copper emitted in the exhaust from gasoline powered automobiles has been measured to be 0.001–0.003 mg/mile driven; 0.005–0.039 mg/mile driven for diesel powered vehicles (Cadle et al. 1999)

Only in a few cases has the form of copper released into the air been determined. In general, metals released into the atmosphere will be in particulate matter in the form of an oxide, sulfate, or carbonate. Because copper smelters co-emit SO<sub>x</sub> gases, copper is expected to be released largely as the sulfate in particulate matter from these facilities. Combustion processes are reported to release copper into the atmosphere as the oxide, elemental copper, and adsorbed copper. Cupric oxide has been identified in emissions from steel manufacturing and in fly ash from oilfired power plants and open-hearth steel mills (Graedel 1978; Perwak et al. 1980). Copper associated with fine particles (<1 µm) tends to result from combustion and other high-temperature sources, while that associated with large particles (>10 µm) is likely to originate from wind blown soil and dust (Schroeder et al. 1987).

Copper has been identified in air samples collected from 38 of the 884 NPL hazardous waste sites where copper has been detected in environmental media. Copper was detected in offsite air samples at concentrations ranging from 0.02–10 µg/m<sup>3</sup> (median concentration of 0.38 µg/m<sup>3</sup>) (HazDat 2002).

### 6.2.2 Water

Much of the copper that enters environmental waters will be associated with particulate matter. Copper is a natural constituent of soil and will be transported into streams and waterways in runoff either due to natural weathering or disturbed soil. Sixty-eight percent of releases to water is estimated from this source. Copper sulfate use represents 13% of releases to water, and urban runoff contributes 2% (Perwak et al. 1980). In the absence of specific industrial sources, runoff is the major factor contributing to elevated copper levels in river water (Nolte 1988). In the EPA-sponsored National Urban Runoff Program, in which 86 samples of runoff from 19 cities throughout the United States were analyzed, copper was found in 96% of samples, at concentrations of 1–100 µg/L (ppb) (Cole et al. 1984). Of the 71 priority pollutants analyzed for, copper, along with lead and zinc, was the most frequently detected. The geometric mean copper concentration in runoff water was 18.7 µg/L.

Yang et al. (1993) provided estimates of global anthropogenic and natural copper inputs into oceans that are derived from two sources, atmospheric deposition and riverine input. Atmospheric input has been estimated at 14–45x10<sup>6</sup> kg/year for copper in a dissolved form and 2–7x10<sup>6</sup> kg/year for copper in a

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particulate form. Riverine input is estimated to be  $10 \times 10^6$  kg/year as dissolved copper and  $1,500 \times 10^6$  kg/year as copper bound to particulates.

Domestic waste water is the major anthropogenic source of copper in waterways (Isaac et al. 1997; Nriagu and Pacyna 1988). Studies in Cincinnati and St. Louis showed discharges of copper into sewer systems from residential areas to be significant, with an average loading of 42 mg/day/person (Perwak et al. 1980). In a more comprehensive review, Jenkins and Russell (1994) reported a range of average copper loadings derived from residential and some small industrial contributions of 2.8–83 mg/capita/day. Concentrations of copper in influents to 239 waste water treatment plants (12,351 observations) were 0.0001–36.5 ppb, and the median value was ~0.4 ppb (Minear et al. 1981). Copper is not entirely removed in POTWs, and releases from these facilities contribute ~8% of all copper released to water (Perwak et al. 1980). Inputs into the Narraganset Bay, Rhode Island, in decreasing order of importance, are sewage effluent, rivers, urban runoff, and atmospheric fallout (Mills and Quinn 1984; Santschi et al. 1984). Ninety percent of both dissolved and particulate copper was from effluent of sewage treatment plants that discharged into the Providence River.

While copper is removed from the waste stream by sewage treatment facilities, considerable copper remains in the effluent and is released into receiving waters (EPA 1981; Perwak et al. 1980). Because removal efficiencies for copper from waste streams tend to remain constant, increases in copper concentrations in POTW influent streams will also result in increased copper concentrations in the effluent streams (Isaac et al. 1997). The range of removal efficiencies reported for pilot and full scale plants suggests that removal depends strongly on plant operation or influent characteristics. The median copper concentrations in domestic waste water have been found to make up a substantial fraction of the median concentration found in POTW influent in the waste water systems of four Massachusetts municipalities, with ratios ranging from 0.36 to 1.25 (Isaac et al. 1997).

A source of copper released to waterways is urban storm water runoff. Copper in storm water runoff originates from the sidings and roofs of buildings, various emissions from automobiles, and wet and dry depositional processes (Davis et al. 2001). Concentrations of between 1 and 100  $\mu\text{g/L}$  of copper in storm water runoff have been measured (Georgopoulos et al. 2001). Storm water runoff normally contributes approximately 2% to the total copper released to waterways. In contrast, copper in runoff that is obtained from the natural weathering of soil or is release from disturbed soils contributes 68% of the copper released to waterways (Georgopoulos et al. 2001).

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The best data on typical POTWs using secondary treatment are that 55–90% of copper is removed in these plants with a median and mean removal of 82% (Perwak et al. 1980). By contrast, those plants using only primary treatment had a 37% median removal efficiency. A more recent study focused on heavy metal removal in three POTWs that received primarily municipal sewage and used activated sludge as a secondary treatment. The study looked at removals in both the primary and secondary treatment stage. The average removals of soluble copper and total copper after secondary treatment were 49–82 and 83–90%, respectively. The average copper concentration in the final effluent was 17–102 ppb (Aulenbach et al. 1987; Stephenson and Lester 1987).

Combined sewer outflows are the primary sources of direct and indirect copper pollutants entering estuaries and other coastal areas of the United States (Crawford et al. 1995; Georgopoulos et al. 2001; Huh 1996; Iannuzzi et al. 1997). For example, Crawford et al. (1995) compiled a summary of the sources of various metals and other contaminants into the Newark Bay estuary. The mass loadings of copper into the estuary as a function of source are (in kg/day): municipal treatment systems, 103.4; industry direct discharge, 8.82; combined sewer overflows, 48.0; storm-water runoff, 62.2; tributary flow, 39.1 and indirect charges from the Passaic Valley Commission and Middlesex County Sewerage Authority, 126.5.

Discharges to water from active mining and milling are small, and most of the western operations do not release any water; water is a scarce resource and is recycled (Perwak et al. 1980). Discharges from electroplating operations are either directly to water or indirectly via POTWs. Runoff from abandoned mines is estimated to contribute 314 metric tons annually (Perwak et al. 1980). These discharges are primarily insoluble silicates and sulfides and readily settle out. Releases from copper-containing products may be substantial, but are difficult to predict. Corrosion of copper in plumbing or construction may result in direct discharges or runoff into waterways. Copper and brass production releases relatively little copper to water.

Waste water generated from mining operations comes from seepage, runoff from tailing piles, or utility water used for mine operation. The amount of waste water generated ranges from 0–300 L water/metric ton of ore mined for open pit copper mines and 8–4,000 L water/metric ton of ore mined underground (EPA 1980b). Copper concentrations in waste water from a selected open pit and underground copper mine were 1.05 and 0.87 ppm, respectively. Data regarding copper concentrations in waste water associated with selected concentrating, smelting, and refining operations can be found in EPA (1980b). Drainage from mining operations and abandoned mines has been shown to have an effect on copper

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content in local surface waters (see Table 6-7) with concentrations as high as 69,000 ppb being measured (Rösner 1998).

Results of an EPA industrial effluent survey show that mean and maximum levels of copper in treated waste water from six industries exceeded 1 and 10 ppm, respectively (EPA 1981). These industries and their mean and maximum discharges in ppm are: inorganic chemicals manufacturing (<1.6, 18); aluminum forming (<160, 2,200); porcelain enameling (1.3, 8.8); gum and wood chemicals (1.4, 3.0); nonferrous metals manufacturing (1.4, 27.0); and paint and ink formulation (<1.0, 60.0). Emission factors in nanograms of copper released per L of water outflow have been estimated for various industries. These factors would enable estimation of an industry's copper releases if the discharge volume were known (Nriagu and Pacyna 1988).

Effluents from power plants that use copper alloys in the heat exchangers of their cooling systems discharge copper into the receiving waters (Harrison 1984). The largest discharges occur after start-up and decrease rapidly thereafter. At the Diablo Canyon Nuclear Power Station, a very high start-up discharge containing 7,700 ppb of copper fell to 67 ppb after 24 hours (Harrison 1984). During normal operation at two nuclear power stations, copper levels ranged between 0.6 and 3.3 ppb. Except for after start-up of the cooling system, most of the soluble copper (that which passes through a 0.45  $\mu\text{m}$  filter) discharged was in bound forms (Harrison et al. 1980). During normal operation, <20% of the copper released was in the <1,000 molecular weight fraction, which contains the more available copper species.

Copper sulfate is directly added to lakes, reservoirs, and ponds for controlling algae. However, the copper concentration in the water column generally returns to pretreatment levels within a few days (Effler et al. 1980; Perwak et al. 1980).

One potential source of copper release into waterways is leachate from municipal landfills. However, copper concentrations in leachate obtained from these waste sites have been found to vary widely. For example, copper concentrations in leachate from municipal landfills have been found to range from 0.005 to 1,110 ppm (Christensen et al. 1994; Perwak et al. 1980; Roy 1994). Although copper was measured in these leachates, its origin may not be from copper contained within the waste site, but from the surrounding soils. Cyr et al. (1987) reported that leachate from three municipal landfills in New Brunswick, Canada, did not contain copper concentrations significantly above those in control samples representing the surrounding soil types. Therefore, the emissions of copper from landfills into leachates

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should be made relative to the contribution of copper from surrounding soils, as determined from appropriately selected control samples.

Copper can enter surface waters as a result of agricultural runoff. For example, estimated loading rates of copper into surface water from irrigation water runoff near the Stillwater National Wildlife Refuge ranged from 0.307 to 8.34 mg/hour, depending on what period of the irrigation season samples were taken (Kilbride et al. 1998). The highest concentrations were obtained during the middle period (August through mid-September) of the irrigation season.

Copper has been identified in groundwater samples collected from 788 groundwater samples and 306 surface water samples of the 884 NPL hazardous waste sites where copper has been detected in environmental media. Copper was detected at concentrations ranging from 0.006 to 5.6 ppm (median concentration of 0.103 ppm) in offsite groundwater and 0.00025–590 ppm (median concentration of 0.0282 ppm) in offsite surface water (HazDat 2002).

### 6.2.3 Soil

An estimated 97% of copper released into the environment is to land (Perwak et al. 1980). These are primarily tailings and overburdens from copper mines and tailings from mills. The copper in the tailings represents the portion of copper that could not be recovered from the ore and is generally in the form of insoluble sulfides or silicates (Perwak et al. 1980). These wastes are disposed in mining states. Other releases to land include sludge from POTWs, municipal refuse, and waste from electroplating, iron and steel producers, and discarded copper products (e.g., plumbing, wiring) that are not recycled. The copper content of municipal solid waste is 0.16%; much of this will be landfilled directly or as residues from incineration. Emission factors in milligrams of copper released per gram of solid waste have been estimated for various industries. These factors would enable the estimation of an industry's copper releases in terms of quantity of solid waste discharged. Sludge from sewage treatment plants is a major source of copper released to land (Nriagu and Pacyna 1988). Agricultural products are believed to constitute 2% of the copper released to soil (Perwak et al. 1980). However, even though the largest releases of copper are to land, exposures to human populations to copper in soil are expected to be minimal in comparison to the primary route of exposure through drinking water (see Section 6.5).

Copper has been identified in soil samples collected from 742 soil samples and 361 sediment samples of the 884 NPL hazardous waste sites where copper has been detected in environmental media. Copper was

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detected at concentrations ranging from 0.01 to 182,000 ppm (median concentration of 0.103 ppm) in offsite soils and 0.022–14,000 ppm (median concentration of 43 ppm) in offsite sediments (HazDat 2002).

### 6.3 ENVIRONMENTAL FATE

It is not always possible to separate the environmental fate processes related to transport and partitioning from those related to transformation and degradation for a metal, its various compounds and complexes. Part of this problem is that the form of copper is rarely identified. It is also difficult to determine when a process such as adsorption should be treated as partitioning or transformation, since the formation of strong bonds to an adsorbent may be construed as a transformation to new molecular species. Separating weak and strong adsorption is awkward and not always possible. Deposition and general adsorption of copper are discussed in Section 6.3.1. Speciation, compound formation, and oxidation-reduction are examined in Section 6.3.2.

#### 6.3.1 Transport and Partitioning

##### 6.3.1.1 Ambient Air

Copper is released to the atmosphere in the form of particulate matter or adsorbed to particulate matter. It is removed by gravitational settling (bulk deposition), dry deposition (inertial impaction characterized by a deposition velocity), washout by rain (attachment to droplets within clouds), and rainout (scrubbing action below clouds) (Schroeder et al. 1987). The removal rate and distance traveled from the source will depend on source characteristics, particle size, and wind velocity.

Gravitational settling governs the removal of large particles ( $>5 \mu\text{m}$ ), whereas smaller particles are removed by the other forms of dry and wet deposition. The importance of wet to dry deposition generally increases with decreasing particle size. The scavenging ratio (ratio of the copper concentration in precipitation [ppm] to its air concentration [ $\mu\text{g}/\text{m}^3$ ]) for large particles displays a seasonal dependence that reflects their more effective scavenging by snow than by rain (Chan et al. 1986). Copper from combustion sources is associated with sub-micron particles. These particles remain in the troposphere for an estimated 7–30 days. In that time, some copper may be carried far from its source (Perwak et al. 1980).

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Metal deposition is characterized by large temporal and spatial variability. Estimated copper deposition rates in urban areas are 0.119 and 0.164 kg/ha/year for dry and wet deposition, respectively (Schroeder et al. 1987). Bulk deposition reportedly ranges from 0.002–3.01 kg/ha/year. For rural areas, bulk deposition reportedly ranges from 0.018 to 0.5 kg/ha/year, and wet deposition is 0.033 kg/ha/year. The washout ratio is 114,000–612,000 ( $\mu\text{g}/\text{m}^3$  rain)/( $\mu\text{g}/\text{m}^3$  air) or, expressed on a mass basis, 140–751 ( $\mu\text{g}/\text{kg}$  rain)/( $\mu\text{g}/\text{kg}$  air). In southern Ontario, Canada, where the average concentration of copper in rain was 1.57 ppb during 1982, 1.36 mg of copper was deposited annually per square meter as a result of wet deposition (Chan et al. 1986). For central and northern Ontario, the mean concentrations of copper in rain were 1.36 and 1.58 ppb, respectively, and the annual wet depositions averaged in both instances 1.13 mg/m<sup>2</sup>.

For the majority of the time, the concentration of toxic trace compounds, like copper, approach regional background levels with only episodic increases, depending on wind speed and direction and location relative to local point sources; smelters are primary source of copper in this study (East St. Louis) (Sweet et al. 1993). Copper depositional fluxes follow an exponential decay curve as one transitions from urban to rural settings. Soil is not the major source of copper in cities or nearby rural soils, but is the predominant source for copper in the atmosphere over more remote areas (Fergusson and Stewart 1992). Sources of copper in urban areas include coal, soil, tire wear, and automobile emissions (Kim and Fergusson 1994). Copper emission from combustion processes is typically associated with fine particles; however, there can be instances where the highest concentrations of copper are measured in coarse particles, thus giving the impression that the copper is derived from crustal sources (Paode et al. 1998).

Depositional fluxes of copper over Chicago have been observed to average between 0.06 mg/m/day, 0.01 mg/m/day over Lake Michigan, and 0.007 mg/m/day over South Haven, Michigan (Paode et al. 1998). Estimated depositional velocities for fine particles (<2.5  $\mu\text{m}$ ) and coarse particles (2.5–10  $\mu\text{m}$ ) in urban (Chicago) and rural (Kankalee, Illinois) areas have been made (Pirrone and Keeler 1993). These are: urban, 0.25–0.46 cm/second and rural, 0.18–0.25 in (rural) Kankalee, Illinois for fine particles; and urban, 1.47–2.93 cm/second and rural, 0.87–1.71 cm/second. The differences in velocities are due to higher surface roughness and wind velocities in Chicago. Combined (dry+wet) deposition of copper has been determined for Massachusetts Bay, with a value of 3,500  $\mu\text{g}/\text{m}^2/\text{year}$  (Golomb et al. 1997). Landing et al. (1995) have reported combined (dry+wet) deposition ranging from 430 to 1,840  $\mu\text{g}/\text{m}^2/\text{year}$  in Florida, whereas Scudlark et al. (1994) have reported a wet copper flux in Chesapeake Bay of 260  $\mu\text{g}/\text{m}^2/\text{year}$ .

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Copper concentrations in particulates formed from the combustion of waste oil are (in  $\mu\text{g/g}$ ):

$687 \pm 11$  ( $10 \mu\text{m}$ ),  $575 \pm 8$  ( $50 \mu\text{m}$ ),  $552 \pm 12$  ( $100 \mu\text{m}$ ),  $568 \pm 9$  ( $300 \mu\text{m}$ ), and  $489 \pm 8$  ( $500 \mu\text{m}$ ).

Approximately 25% of copper is in the  $10 \mu\text{m}$  fraction and 18% is in each of the larger fractions (Nerín et al. 1999).

### 6.3.1.2 Ambient Waters

The average concentrations of copper in Lakes Superior, Erie, and Ontario are 760, 870, and 830 ng/L, respectively (Georgopoulos et al. 2001; Nriagu et al. 1996). The atmospheric input of copper into the Great Lakes is substantial, 330–1,470 ng/m<sup>2</sup>/year, and accounts for 60–80% of the anthropogenic input into Lake Superior and 20–70% into Lakes Erie and Ontario. The mean residency times of copper in sediments are estimated to be 15 years in Lake Erie and 101 years in Lake Superior.

Much of the copper discharged into waterways is in particulate matter and settles out, precipitates out, or adsorbs to organic matter, hydrous iron and manganese oxides, and clay in sediment or in the water column. A significant fraction of the copper is adsorbed within the first hour, and in most cases, equilibrium is obtained within 24 hours (Harrison and Bishop 1984). In fact, most of the copper in POTW effluent and surface runoff is already complexed (Sedlak et al. 1997). Copper in waste water discharged into a river leading into Chesapeake Bay, Maryland, contained 53 ppb of copper, of which 36 ppb was in the form of settleable solids (Helz et al. 1975). The concentration of copper rapidly decreased downstream of the outfall; 2–3 km from the outfall, the copper concentration had fallen to 7 ppb. The concentration of copper in sediment downstream from the outfall was about a factor of 10 higher than in uncontaminated areas.

Copper binds primarily to organic matter in estuarine sediment, unless the sediment is organically poor. A study evaluated the importance of different nonlithogenic components of aerobic estuarine sediment to copper by determining copper's adsorptivity to model sedimentary phases from artificial seawater (Davies-Colley et al. 1984). These phases included hydrous iron and manganese oxides, clay, aluminosilicates, and organic matter. The binding affinities varied by over a factor of 10,000 and were in the following order: hydrous manganese oxide > organic matter > hydrous iron oxide > aluminosilicates > clay (montmorillonite). The partition coefficients at pH 7 for the more strongly bound phases (manganese oxide, iron oxide, and estuarine humic material), were 6,300, 1,300, and 2,500, respectively. The affinity increased somewhat with pH, but did not vary appreciably when salinity was reduced. Considering the compositional characteristics of estuarine sediment, the results indicate that copper binds predominantly

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to organic matter (humic material) and iron oxides. Manganese oxide contributes only 1% to the binding because of its low concentration in sediment; the other phases are generally unimportant. These findings concur with results of selective extraction experiments (Badri and Aston 1983) and the association of copper with humic material (Raspor et al. 1984).

**6.3.1.3 Ambient Soils**

Most copper deposited in soil from the atmosphere, agricultural use, and solid waste and sludge disposal will be strongly adsorbed and remain in the upper few centimeters of soil, except in sandy soils where the lability of bound copper is greater. Copper's movement in soil is determined by a host of physical and chemical interactions of copper with the soil components. In general, copper will adsorb to organic matter, carbonate minerals, clay minerals, or hydrous iron and manganese oxides (EPA 1979; Fuhrer 1986; Janssen et al. 1997; Petruzzelli 1997; Tyler and McBride 1982). Sandy soils with low pH have the greatest potential for leaching. Luncan-Bouché et al. (1997) have shown that between 55 and 85% of copper bound to sand is remobilized upon reduction of the pH from 9 to 4. In most temperate soils, the pH, organic matter, concentrations of metal oxyhydroxides, and ionic strength of the soil solutions are the key factors affecting adsorption (Elliot et al 1986; Fuhrer 1986; Gerritse and Van Driel 1984; Janssen et al. 1997; Rieuwerts et al. 1998; Tyler and McBride 1982). The ionic strength and pH of the soil solution affect the surface charge of soils and thereby influence ionic interaction (Rieuwerts et al. 1998). When the amount of organic matter is low, the mineral content of Fe, Mn, and Al oxides become important in determining the adsorption of copper. Fuhrer (1986) reported that, in oxidized estuarine sediment, adsorption of copper is dominated both by amorphous iron oxide and estuarine humic material.

Copper binds to soil much more strongly than other divalent cations, and the distribution of copper in the soil solution is less affected by changes in pH (within the range of pHs normally encountered in the environment) than other metals are (Gerritse and Van Driel 1984). In a study of competitive adsorption and leaching of metals in soil columns of widely different characteristics, copper eluted much more slowly and in much lower quantities than Zn, Cd, and Ni from two mineral soils and not at all from peat soil, which contained the greatest amount of organic matter (Tyler and McBride 1982). Elliot et al. (1986) looked at pH-dependent adsorption of the bivalent transition metal cations (Cd, Cu, Pb, and Zn) in two mineral soils and two soils containing considerable organic matter. Adsorption increased with pH, and Cu and Pb were much more strongly retained than Cd and Zn. Reduction in absorptivity after removal of the organic matter demonstrated the importance of organic matter in binding copper. However, in a study of clay soils, Wu et al. (1999) observed that although there was a preference for

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copper binding to organic matter in the overall clay soil, higher copper retentions were obtained in the fine (<0.2  $\mu\text{m}$ ) clay fractions once the organic matter had been removed.

To determine the factors affecting copper solubility in soil, Hermann and Neumann-Mahlkau (1985) performed a study in the industrial Ruhr district of West Germany, which has a high groundwater table (10–80 cm from the surface) and a history of heavy metal pollution. Groundwater samples were taken from six locations and two horizons of soil, an upper oxidizing loam, and a lower reducing loam. Total copper concentrations were high in the upper soil horizons and low in the lower horizons. Copper showed a pronounced solubility only in the oxidizing environment; in the reducing environment, solubility was low, possibly due to the formation of sulfides.

The form of copper at polluted and unpolluted sites may affect its leachability, particularly by acid rain. The leaching of heavy metals by simulated acid rain (pH 2.8–4.2) was measured by applying rainwater to columns containing humus layers from sites in a Swedish spruce forest both near to and far from a brass mill (Strain et al. 1984). Leaching of copper increased considerably when water with a pH <3.4 was applied to soil from polluted sites. Acid rain produced from  $\text{SO}_x$  emitted from smelters may increase the leachability of copper in areas affected by smelter stack emissions. Mobility of copper from soils was also found to increase upon introduction of deicing salts into soil, due to the increased mobilization of organic matter in soils, especially in soils with high exchangeable Na and low electrolyte concentrations (Amrhein et al. 1992).

Since 25–75% of copper entering POTWs is removed in sludge, much of which is disposed of by spreading on land, it is important to ascertain whether copper in sludge is apt to leach into soil. This does not appear to be the case; leachate collected from sludge-amended soil contained <12 ppb of copper (Perwak et al. 1980). In laboratory experiments, three sludges containing 51, 66, and 951 ppm (dry weight) of copper were applied to soil columns containing four coastal plain soils. The columns were subsequently leached with distilled water at a rate of 2.5 cm/day for a total column application of 25.4 cm of water. Only small amounts (<0.01–0.87 ppm) of copper were found in the leachate (Ritter and Eastburn 1978). This indicates that hazardous amounts of copper should not leach into groundwater from sludge, even from sandy soils. In another study, soil cores taken after sewage sludge was applied to grassland for 4 years showed that 74 and 80% of copper remained in the top 5 cm of a sandy loam and calcareous loam soil (Davis et al. 1988). Similar studies have also shown that copper is typically confined to the upper 5–10 cm of sludge-amended agricultural soils (Breslin 1999; Giusquiani et al. 1992). In soils receiving long-term, heavy applications of sludge, high copper concentrations (471 mg/kg

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in comparison to 19.1 mg/kg in unamended control soils) were reported to depths of up to 25 cm (Richards et al. 1998). The mobility of copper into soil from sludge was found to be determined mainly by the amount of soil organic carbon and soil surface area (Domergue and Védy 1992; Gao et al. 1997). In addition, soils amended by sludge with low metal content were found to have increased sorption for copper due to the increased binding capacity provided by the “low metal” organics in the sludge (Petruzzelli et al. 1994).

Similarly, copper remains in the surface layer when it is applied to soil as a liquid. Secondary sewage effluent spiked with 0.83 ppm of copper was applied weekly to four different soils. After 1 year of treatment, the concentration of copper in the surface horizons increased greatly; 50–76% of applied copper was found in the upper 2.5 cm and 91–138% was found in the upper 12.7 cm (Brown et al. 1983). In a study of accumulation and movement of metal in sludge-amended soils, field plots received massive amounts of sewage over a period of 6 years. Two sludges (one containing industrial waste), with average copper contents of 0.29 and 23 ppm were incorporated into the top 20 cm of soil in the spring; barley was grown, and after harvest, core samples of soil taken down to 1 m. Some movement of copper into the 22.5–25 cm layer of soil was observed, but little, if any, below this zone. However, at this depth, the copper is still within the root zone of many important food crops and is therefore available for uptake into these plants. Also, the availability of the copper in soil, as determined by its extractability with diethylenetriamine pentaacetic acid (DTPA) and nitrate, remained constant over a 4-year period at all depths. From the results of other work, it is expected that the major portion of the copper (40–74%) is associated with the organic, Fe-Mn-oxide and carbonate fractions of most soils (Ma and Rao 1997).

#### 6.3.1.4 Bioconcentration and Biomagnification

The bioconcentration factor (BCF) of copper in fish obtained in field studies is 10–100, indicating a low potential for bioconcentration. The BCF is higher in molluscs, especially oysters, where it may reach 30,000 (Perwak et al. 1980). This may be due to the fact that they are filter feeders, and copper concentrations are higher in particulates than in water. However, there is abundant evidence that there is no biomagnification of copper in the food chain (Perwak et al. 1980). A study was conducted with white suckers and bullheads, both bottom-feeding fish, in two acidic Adirondack, New York, lakes (Heit and Klusek 1985). These lakes were known to have received elevated loadings of copper, but the suckers and bullhead had average copper levels of only 0.85 and 1.2 ppm (dry weight) in their muscle tissue. The biomagnification ratio (the concentration of copper in the fish to that in potential food) was <1, indicating no biomagnification in the food chain. Similarly, the copper content of muscle tissue of fish from copper-

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contaminated lakes near Sudbury, Ontario, did not differ significantly from that of fish in lakes far from this source (Bradley and Morris 1986).

Diks and Allen (1983) added copper to four sediment/water systems and studied the distribution of copper among five geochemical phases. The investigators then attempted to correlate the concentration in each phase with the copper uptake by tubificid worms. Only copper extracted from the manganese oxide/easily-reducible phase correlated with the copper content of worms at the 95% confidence level.

No evidence of bioaccumulation was obtained from a study of pollutant concentrations in the muscle and livers of 10 mammal species in Donana National Park in Spain (Hernandez et al. 1985). The animals were classified into three categories (herbivorous, omnivorous, and carnivorous) to ascertain if the pollutants were showing biomagnification in higher trophic levels of animals. No evidence of copper biomagnification in the food chain was observed. A study of heavy metals in cottontail rabbits on mined land treated with sewage sludge showed that, while the concentration of copper in surface soil was 130% higher than in a control area, the elevation was relatively little in foliar samples. No significant increase in copper was observed in rabbit muscle, femur, kidney, or liver, indicating that copper was not bioaccumulating in the food chain (Dressler et al. 1986). Even at the lowest levels of the food chain, there is little evidence of copper bioaccumulation. In a study of earthworms and soil from 20 diverse sites in Maryland, Pennsylvania, and Virginia, copper concentrations in earthworms poorly correlated with that in soil (Beyer and Cromartie 1987).

### 6.3.2 Transformation and Degradation

#### 6.3.2.1 Air

Few data are available regarding the chemical forms of copper in the atmosphere and their transformations. In the absence of specific information, it is generally assumed that metals of anthropogenic origin, especially those from combustion sources, exist as oxides. Metallic species are attacked by atmospheric oxidants in the atmosphere, resulting in the formation of oxides. As these oxides age, sulfatization may occur, but only when  $\text{SO}_x$  gases are co-emitted. For example, in Arizona, atmospheric copper originating from smelters was strongly correlated with sulfur (Schroeder et al. 1987).

In fogwater, Cu(II) is reduced to Cu(I) by sulfite and is enhanced by the fact that sulfite is also a ligand for Cu(I) (Xue et al. 1991). Concentrations of Cu(I) in fogwater ranged between 0.1 and 1  $\mu\text{M}$ , which

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amounted to 4 and >90% of copper in the Cu(I) state. The reduction of Cu(II) to Cu(I) is pH dependent and occurs rapidly at pHs>6 (Xue et al. 1991)

**6.3.2.2 Water**

The Cu(I) ion is unstable in aqueous solution, tending to disproportionate to Cu(II) and copper metal unless a stabilizing ligand is present (EPA 1979; Kust 1978). The only cuprous compounds stable in water are insoluble ones such as Cu<sub>2</sub>S, CuCN, and CuF. In its Cu(II) state, copper forms coordination compounds or complexes with both inorganic and organic ligands. Ammonia and chloride ions are examples of species that form stable ligands with copper. Copper also forms stable complexes with organic ligands such as humic acids, binding to -NH<sub>2</sub> and -SH groups and, to a lesser extent, with -OH groups. Natural waters contain varying amounts of inorganic and organic species; this affects the complexing and binding capacity of the water and the types of complexes formed. In seawater, organic matter is generally the most important complexing agent (Coale and Bruland 1988). The formation of ligands may affect other physicochemical processes such as adsorption, precipitation, and oxidation-reduction in water (EPA 1979).

The major species of soluble copper found in freshwater, seawater, and a combination of the two over a range of pHs is Cu<sup>2+</sup>, Cu(HCO<sub>3</sub>)<sup>+</sup>, and Cu(OH)<sub>2</sub> (Long and Angino 1977). At the pH values and carbonate concentrations characteristic of natural waters, most dissolved Cu(II) exists as carbonate complexes rather than as free (hydrated) cupric ions (Stiff 1971).

The concentration of dissolved copper depends on factors such as pH, the oxidation-reduction potential of the water, and the presence of competing cations (Ca<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>, etc.), salts (OH<sup>-</sup>, S<sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>), and anions of insoluble cupric and organic and inorganic complexing agents. If the concentration of a particular anion is high enough to exceed the solubility of a copper salt, precipitation of that salt will occur. The most significant precipitate formed in natural waters is malachite (Cu<sub>2</sub>[OH]<sub>2</sub>CO<sub>3</sub>); other important precipitates are Cu(OH)<sub>2</sub> (and ultimately CuO) and azurite (Cu<sub>3</sub>[OH]<sub>2</sub>[CO<sub>3</sub>]<sub>2</sub>) (Sylva 1976). In anaerobic waters, Cu<sub>2</sub>S, Cu<sub>2</sub>O, and metallic copper forms and settles out (EPA 1979). The combined processes of complexation, adsorption, and precipitation control the level of free Cu(II). The chemical conditions in most natural water are such that, even at relatively large copper concentrations, these processes will reduce the free Cu(II) concentration to extremely low values.

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As a result of all of the aforementioned physico-chemical processes, copper in water may be dissolved or associated with colloidal or particulate matter. Copper in particulate form includes precipitates, insoluble organic complexes, and copper adsorbed to clay and other mineral solids. In a survey of nine rivers in the United Kingdom, 43–88% of the copper was in the particulate fraction (Stiff 1971). A study using suspended solids from the Flint River in Michigan found that the fraction of adsorbed copper increased sharply with pH, reaching a maximum at a pH of 5.5–7.5 (McIlroy et al. 1986).

The colloidal fraction may include hydroxides and complexes with amino acids. The soluble fraction is usually defined as that which will pass through a 0.45  $\mu\text{m}$  filter; it includes free copper and soluble complexes as well as fine particulates and colloids. The soluble fraction may be divided according to the lability of the copper forms in the water. Categories range from the very labile (e.g., free metal ion) to nonlabile (e.g., colloidally bound) metal (Tan et al. 1988). Various techniques may be used to classify the lability of different fractions of soluble copper; these techniques include solvent extraction, ion-specific electrodes, ion exchange, ultrafiltration, electrochemical methods such as anodic stripping voltammetry, and gel filtration chromatography (Harrison and Bishop 1984). The resulting classification depends on the specific procedure employed; therefore, it is not possible to compare the results of different researchers, except in general terms. In a typical study, 18–70% of dissolved copper in river water was moderately labile and 13–30% was slowly labile (Tan et al. 1988).

The nature of copper's association with inorganic and organic ligands will vary depending on the pH, copper concentration, concentration of competing ligands in the body of water, binding capacity of the ligands, and hardness or salinity of the water (Breault et al. 1996; Cao et al. 1995; Gardner and Ravenscroft 1991; Giusti et al. 1993; Lores and Pennock 1998; Town and Filella 2000). In river water from the northwestern United States that had a relatively high pH (7.0–8.5) and alkalinity (24–219 ppm as  $\text{CaCO}_3$ ), inorganic species like  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  were the most important ligands at high copper concentrations. However, other species were important at low copper concentrations. On the other hand, samples from lakes and rivers in southern Maine with a relatively low pH (4.6–6.3) and alkalinity (1–30 ppm as  $\text{CaCO}_3$ ) were largely associated with organic matter. The binding of copper to dissolved organics was found to be dependent on the specific chemical species (e.g., fulvic acid and EDTA) and their concentrations in the surface water, the number of binding sites per fulvic acid carbon, and the hardness of the water (Breault et al. 1996). Increasing water hardness results in decreased fulvic acid binding sites; this effect is due more to the suppression of high molecular weight fulvic acid solubility in the presence of Ca and Mg ions than to competition of these ions with copper for the fulvic acid binding

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sites. Increasing pH from 8 to 6 resulted in a 7-fold increase in the conditional binding constant for Cu(II) with humic acid (Cao et al. 1995).

The extent to which copper binds to inorganic and organic ligands can be altered by materials carried in runoff. For example, after a period of rain in southeastern New Hampshire, inorganic constituents contributed more to the copper binding in lakes and rivers than did dissolved organic matter (Truitt and Weber 1981). Runoff induced by the rain had added to the inorganic load of the rivers and lakes, as was evidenced by their pH (5.7–7.4) and alkalinity (1.7–43.4 ppm as CaCO<sub>3</sub>). A green precipitate, confirmed to be malachite (Cu<sub>2</sub>[OH]<sub>2</sub>CO<sub>3</sub>) was formed in river water in Exeter; this water had the highest pH and alkalinity. A computer simulation of the copper species in pond water and artesian well water that fed the pond predicted that 98% of the copper in the artesian well water would be bound to organic matter, whereas 88 and 63% of the copper in pond water would be bound to organics in the spring and fall, respectively (Giesy et al. 1983).

Seawater samples obtained in a transect of the uppermost Narragansett Bay in August 1980 were analyzed for dissolved, particulate, and organically bound copper to investigate the geochemistry of copper-organic complexes (Mills and Quinn 1984). Narragansett Bay is a partly mixed estuary in Massachusetts and Rhode Island that receives organic matter and metals from rivers, municipal and industrial effluents, and runoff. Dissolved copper represented 60% of the total copper and ranged from 16.4 µg/kg in the Providence River to 0.23 µg/kg in Rhode Island Sound. Analysis of the data indicated that . 75% of this copper is removed within the Providence River. Particulate copper concentrations ranged from 2.42 to 0.06 µg/kg and generally comprised 40% of the total copper. Fourteen to 70% (0.12–2.30 µg/kg) of the dissolved copper was complexed with organic matter.

Organic ligands may contain a variety of binding sites, and the strength of the resulting copper complexes will vary accordingly. Over 99.7% of the total dissolved copper in surface ocean water from the northeast Pacific was associated with organic ligands (Coale and Bruland 1988). The dominant organic complex, limited to surface water, was a strong ligand of biogenic origin. A second, weaker class of organic ligand was of geologic origin. An independent study showed the copper binds to humic material at a number of sites; the binding strength of the sites varied by two orders of magnitude (Giesy et al. 1986). The humic material in the study was derived from nine surface waters in the southeastern United States. Soluble copper in water discharged from a nuclear power station was primarily complexed with organic matter in the 1,000–100,000 molecular weight range (Harrison et al. 1980). Ten to 75% of the discharged copper was in particulate form.

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The bioavailability of Cu(I) has been largely ignored since soluble or complexed forms of copper in this oxidation state have not been thought to occur in significant amounts in aerobic environments.

Investigators have speculated on the possibility that Cu(II) can be directly or indirectly reduced to Cu(I) by photochemical processes (Moffett and Zika 1987). If this should occur, it would be more likely to occur in seawater, where chloride ions might stabilize the Cu(I) through complex formation. Cu(II)-organic complexes absorb radiation  $>290$  nm and can undergo charge transfer reactions where the Cu(II) is reduced and the ligand is oxidized. Photochemically-generated reducing agents such as  $O_2^-$  and  $H_2O_2$  could also reduce Cu(II) to Cu(I).

Experiments performed in synthetic seawater and water from Biscayne Bay, Florida, showed that in the reduction of Cu(II) to Cu(I), the rate was first-order in  $Cl^-$  and second-order in  $H_2O_2$ . The chloride ion is thought to be required for forming stable  $CuClOH^-$ . Experiments showed that as much as 15% of copper in seawater was as Cu(I). Additionally, sunlight increases the percentage of free Cu(II). The photochemical reduction mechanism is supported by the observation that the Cu(I) concentration is highest in the surface layer of seawater and that the hydrogen peroxide concentration increases in parallel to that of Cu(I) (Moffett and Zika 1987). In addition, the percentage of free Cu(II) is highest on the surface.

Once Cu(I) is formed, its lifetime is determined by its rate of oxidation to Cu(II). After Biscayne Bay water was exposed to sunlight for 5 hours, the Cu(I) formed was oxidized to Cu(II); the half-life of the Cu(I) was 12 hours. Dissolved oxygen is primarily responsible for this reaction. Since the oxidation of Cu(I) by  $O_2$  in distilled water occurs in  $<6$  minutes, the Cu(I) apparently is stabilized in seawater by the formation of complexes. In the presence of humic acids, the oxidation of Cu(I) occurs very rapidly. In coastal water off the Everglades in Florida, no Cu(I) was detected, due to the tying up of Cu(II) in organic complexes and the high concentration of radical oxidants in the water. Sharma and Millero (1988) measured the rate of Cu(I) oxidation in seawater as a function of pH, temperature, and salinity. The rate of reaction increased with pH and temperature, and decreased with increasing ionic strength (or salinity). The results suggested that the rates are controlled by  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Cl^-$ , and  $HCO_3^-$  through their involvement in complex formation and ligand exchange.

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**6.3.2.3 Sediment and Soil**

The adsorption of copper to soil and sediment has been discussed in Section 6.3.1 under transport and partitioning, even though adsorption may really be complexation and transformation. Between pH 5 and 6, adsorption is the principal process for removing copper from water; above pH 6, precipitation becomes more dominant (Perwak et al. 1980). Copper binding in soil may be correlated with pH, cation exchange capacity, the organic content of the soil, the presence of manganese and iron oxides, and even the presence of inorganic carbon such as carbonates (Petruzzelli 1997; Rieuwerts et al. 1998). However, broad generalizations about the lability of copper in soils are not possible since the situation will differ among different soil types and environmental conditions.

The form of copper in soil is determined by measuring the extractability of the copper with different solvents. This extractability is determined by the nature of the soil and the form of copper deposited in the soil. If a relatively labile form of copper is applied, binding to inorganic and organic ligands may occur, as well as other transformations. On the other hand, if a mineral form is deposited, it would be unavailable for binding. The capacity of soil to remove copper and the nature of the bound copper were evaluated by incubating 70 ppm of copper with 5 g samples of soil for 6 days (King 1988). Twenty-one samples of soils (10 mineral and 3 organic) from the southeastern United States were included in the study. Some soil samples were taken from the subsoil as well as the surface. The amount of adsorbed copper ranged from 36 to 100%, of which 13–100% was nonexchangeable when extracted with KCl. Removal of copper from solution was much higher with surface soils than with subsurface sandy soils; 95–100% of the copper was removed by five mineral surface soils and all three organic soils. The percentage of copper that was nonexchangeable was relatively high in all but some of the acid subsoils. While the fraction of exchangeable copper was not dependent on pH in surface soils, 96% of the variation in exchangeability was correlated with pH in subsoils. The soil/water partition coefficient for copper was  $>64$  for mineral soils and  $>273$  for organic soils. Of the eight heavy metals in the study, only Pb and Sb had higher partition coefficients than copper. Most of the copper in Columbia River estuary sediment and soil was correlated with inorganic carbon (e.g., carbonate), but not with the amount of extractable Fe or the organic carbon content of the sediment (Fuhrer 1986).

The amount of ammonium acetate- and DTPA-extractable copper in wetland soil/sediment resulting from atmospheric deposition from smelters in Sudbury, Ontario, showed the same pattern as total copper, despite random variations in soil pH, redox potential, and organic carbon (Taylor and Crowder 1983). Therefore, in this case, soil characteristics were not the dominant factors determining extractability and

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availability, but rather the form of copper that was deposited. The median concentrations of total copper, ammonium acetate-extractable copper, and DTPA-extractable copper at 25 sample sites were 371, 49, and 98 ppm, respectively.

In another study, copper fractionation in nine different contaminated soils, sequential extractions were used to operationally define six soil fractions in decreasing order of copper availability; water soluble > exchangeable > carbonate > Fe-Mn oxide > organic > residual (Ma and Rao 1997). The results of this study showed that distribution of copper in these six soil fractions differed depending on the total copper concentration in the soil. As the copper concentration increased above 240 mg/kg, between 69 and 74.4% of the total copper was found in the water soluble, carbonate, Fe-Mn oxide, and organic fractions. In relatively uncontaminated soils (<240 mg/kg copper), between 97.6 and 99.6% of the copper was found to be associated with the residual fraction.

Within the estuarine environment, anaerobic sediments are known to be the main reservoir of trace metals. Under anaerobic conditions, cupric salts will reduce to cuprous salts. The precipitation of cuprous sulfide and the formation of copper bisulfide and/or polysulfide complexes determine copper's behavior in these sediments (Davies-Colley et al. 1985). In the more common case where the free sulfide concentration is low due to the controlling coexistence of iron oxide and sulfide, anaerobic sediment acts as a sink for copper. However, in the unusual situation where the free sulfide concentration is high, soluble cuprous sulfide complexes may form, and the copper concentration in sediment pore water may then be high.

In sediment, copper is generally associated with mineral matter or tightly bound to organic material (Kennish 1998). As is common when a metal is associated with organic matter, copper is generally associated with fine, as opposed to coarse, sediment. Badri and Aston (1984) studied the association of heavy metals in three estuarine sediments with different geochemical phases. The phases were identified by their extractability with different chemicals and termed easily or freely leachable and exchangeable; oxidizable-organic (bound to organic matter); acid-reducible (Mn and Fe oxides and possibly carbonates); and resistant (lithogenic). In the three sediments, the nonlithogenic fraction accounted for 14–18% of the total copper, and the easily exchangeable component was 5% of the total copper. Sediment samples taken from western Lake Ontario were similarly analyzed in regard to the compositional associations of copper by a series of sequential extractions (Poulton et al. 1988). The mean and standard deviation percentages of copper in the various fractions were: exchangeable, 0 (0); carbonate, 0.1 (0.3); iron or manganese oxide-bound, 0.2 (0.3); organic-bound, 40 (11); and residual, 60 (8). Another study found

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that 10–20% of the copper in Lake Ontario sediment samples was bound to humic acids, and virtually all of the copper was bound to organic matter (Nriagu and Coker 1980). The concentration of copper associated with humic acids was 21–40 times greater than in the sediment as a whole.

### 6.3.2.4 Other Media

Copper is an essential nutrient in plant metabolism. Therefore, uptake of copper from soil in plants through the roots is a natural and necessary process, a process that is actively regulated by the plant (Clemens 2001). The uptake of copper into plants is dependent on the concentration and bioavailability of copper in soils. The bioavailability of copper is determined largely by the equilibrium between copper bound to soil components and copper in soil solution. As noted in the discussion of copper binding in soils (Section 6.3.1.3), this is determined by copper concentrations in soil, soil type, soil components, pH, oxidation-reduction potential in the soil, and concentrations of other cations and anions in the soil, etc. (Rieuwerts et al. 1998). Other factors include root surface area, plant genotype, stage of plant growth, weather conditions, interaction with other nutrients in the soil, and water table (Gupta 1979). Liming is another factor that affects copper uptake. For example, liming acidic soils has been shown to increase copper uptake in hay, but to decrease copper uptake in wheat (Gupta 1979). However, the effect that liming has on increasing soil pH does not appear to be the overriding mechanism behind the changes in copper uptake in plants, even though there is evidence that the addition of lime to soil to increase the pH to 7 or 8 reduces copper availability to plants (Perwak 1980). This is evidenced by the fact that changes in pH (5.4–8.0) have been found to have little effect on copper concentrations in plant tissues (Gupta 1979).

## 6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

### 6.4.1 Air

The concentrations of copper in air depend on the proximity of the site to major sources such as smelters, power plants, and incinerators. The results of several studies in which concentrations of copper in air were reported appear in Table 6-5.

According to the EPA's National Air Surveillance Network report for the years 1977, 1978, and 1979, median copper concentrations were 133, 138, and 96 ng/m<sup>3</sup>, respectively, for urban samples and 120, 179, and 76 ng/m<sup>3</sup> for nonurban samples, respectively (Evans et al. 1984). In this study, 10,769 urban and

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1,402 nonurban air samples collected for 24 hours were analyzed. For 1977, 1978, and 1979, 1% of urban samples exceeded 1,156, 975, and 843 ng/m<sup>3</sup>, respectively, and 1% of nonurban samples exceeded 1,065, 1,396, and 645 ng/m<sup>3</sup>, respectively. The maximum urban and nonurban copper concentrations reported were 4,625 and 4,003 ng/m<sup>3</sup>, respectively. Davies and Bennett (1985) reported average atmospheric copper concentrations of 5–50 ng/m<sup>3</sup> in rural areas and 20–200 ng/m<sup>3</sup> in urban locations. The concentrations in rural areas are considerably lower than those reported in the EPA survey. Data from many urban locations in the United States show concentrations of copper associated with particulate matter ranging from 3 to 5,140 ng/m<sup>3</sup> (Schroeder et al. 1987). Remote and rural areas have concentrations of 0.029–12 and 3–280 ng/m<sup>3</sup>, respectively. The levels reported by Schroeder et al. (1987) are consistent with those obtained in a study of airborne trace elements in national parks (Davidson et al. 1985). In the Smokey Mountain National Park, the copper concentration in air was 1.6 ng/m<sup>3</sup>, while in the Olympic National Park, where several locations were monitored, 3.3–6.7 ng/m<sup>3</sup> of copper was measured in the atmosphere. The lower copper concentrations found in Smokey Mountain Park compared with those in the Olympic National Park have been attributed to greater vegetative cover and higher moisture in the former and larger amounts of exposed rock and soil in the latter. Average

**Table 6-5. Concentrations of Copper in Air**

Date/sample	Location	Concentration <sup>a</sup> (ng/m <sup>3</sup> ) (mean) [median]	Comments	Reference
1977, urban	United States	[133], 433 <sub>90</sub> , 1,156 <sub>99</sub> (207.5), 3,296 <sub>max</sub>	4,648 samples, National Survey	Evans 1984
1978, urban	United States	[138], 430 <sub>90</sub> , 975 <sub>99</sub> (200.8), 4,625 <sub>max</sub>	3,615 samples, National Survey	Evans 1984
1979, urban	United States	[96], 363 <sub>90</sub> , 519 <sub>99</sub> (259.3), 1,627 <sub>max</sub>	2,507 samples, National Survey	Evans 1984
1977, nonurban	United States	[120], 450 <sub>90</sub> , 1,065 <sub>99</sub> (193.2), 16,706 <sub>max</sub>	709 samples, National Survey	Evans 1984
1978, nonurban	United States	[179], 607 <sub>90</sub> , 1,396 <sub>99</sub> (265.7), 1,396 <sub>max</sub>	458 samples, National Survey	Evans 1984
1977, nonurban	United States	[76], 322 <sub>90</sub> , 645 <sub>99</sub> (141.7), 4,003 <sub>max</sub>	235 samples, National Survey	Evans 1984
Urban		20–200, [50]	Representative values	Davies and Bennett 1985
Rural		5–50, [20]		
Remote		0.29–12	Values from literature survey	Schroeder et al. 1987
Rural		3–280		
Urban	Canada	17–500		
Urban	United States	3–5,140		
Urban	Europe	13–2,760		
Urban	Other	2.0–6,810		
1979, remote	Smokey Mountain National Park	(1.6)	Above canopy, crustal enrichment factor 31	Davidson et al. 1985

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**Table 6-5. Concentrations of Copper in Air (continued)**

Date/sample	Location	Concentration <sup>a</sup> (ng/m <sup>3</sup> ) (mean) [median]	Comments	Reference
1980, remote	Olympic National Park	3.3–6.7, (5.6)	Crustal enrichment factor 76	Davidson et al. 1985
1981, 1982, summer	Camden, New Jersey	16.0–18.0 <sup>b</sup> , 100.0 <sub>max</sub>	Seasonal variations noted; three urban areas and one rural area.	Liroy et al. 1987
	Elizabeth, New Jersey	21.0–29.0, 120.0 <sub>max</sub>		
	Newark, New Jersey	25.0–33.0, 131.0 <sub>max</sub>		
	Ringwood, New Jersey	13.0–63.0, 77.0 <sub>max</sub>		
1982, 1983, winter	Camden, New Jersey	17.0–21.0, 231.0 <sub>max</sub>		
	Elizabeth, New Jersey	28.0–36.0, 493.0 <sub>max</sub>		
	Newark, New Jersey	21.0–27.0, 380.0 <sub>max</sub>		
	Ringwood, New Jersey	6.0–18.0, 29.0 <sub>max</sub>		

<sup>a</sup>Percentile level and maximum indicated as subscripts.

<sup>b</sup>Concentrations in Liroy et al. (1987) are geometric means, unless otherwise noted.

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copper crustal enrichment factors (the concentration of copper in air compared with the average concentration in the earth's crust) were 31 and 76, respectively.

As part of the Airborne Toxic Element and Organic Substances (ATEOS) project for determining patterns of toxic elements in different settings, three urban areas (Camden, Elizabeth, and Newark) and one rural site (Ringwood) in New Jersey were studied during two summers and winters between 1981 and 1983 (Lioy et al. 1987). Each site was sampled every 24 hours for 39 consecutive days. The geometric mean copper concentrations were 16.0–21.0, 21.0–36.0, 21.0–33.0, and 6.0–63.0 ng/m<sup>3</sup> for Camden, Elizabeth, Newark, and Ringwood, respectively. The levels of copper measured in these industrial urban areas are considerably lower than the mean values reported in the National Air Surveillance survey (201–259 mg/m<sup>3</sup> for 1977–1979 [Evans et al. 1984]). Summer and winter maxima in the three urban areas were 100.0–131.0 and 231.0–493.0 ng/m<sup>3</sup>, respectively, and 77.0 and 29.0 ng/m<sup>3</sup>, respectively, for Ringwood. Copper follows the same pattern as other heavy metals, in that increased copper levels are present in winter in urban areas and in summer in rural areas. No explanation for this pattern has been offered.

Airborne concentrations of copper in the indoor atmosphere average between 8 and 12 ng/m<sup>3</sup> (Koutrakis et al. 1992). The concentration was significantly affected by the use kerosene heaters, which were found to emit copper into the indoor air at a rate of 15,630 ng/hour (Koutrakis et al. 1992).

Anderson et al. (1988) performed a study of the atmospheric aerosols collected at a site in Chandler, Arizona, over a 12-day period in February and March 1982. Several major copper smelters are located 120 km to the southeast. Particles containing >0.5% Cu were termed 'Cu-bearing' particles; 5.6% of the fine (0.4 to 2 μm) particles collected were in this category. The most abundant type of Cu-bearing particle, representing 74% of the total, was associated with sulfur; however, the analysis was not able to specify the form of sulfur present. These particles were often associated with Zn, Fe, Pb, As, and Ca. Sixteen percent of the Cu-bearing particles were associated with silicon and 4% were associated with chloride. The concentration of Cu-S particles was highest when the surface and upperlevel winds were from the southeast to the east, and reached a maximum 1–2 days after the winds began to blow from the southeast; the smelters to the southeast were the probable source. The particles associated with silicon and chlorine did not show any apparent correlation with wind and were either from a diffuse regional source or a local source.

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Mine waste dump sites are a source of airborne copper carried in dust (Table 6-6). Particle size distribution and the concentration of copper in particle size ranges differ depending on the mine waste site (Mullins and Norman 1994). For example, the mean concentrations (ppm, w/w) of copper in dust (<10 µm particle size range) collected at four mine waste dump sites in Butte, Montana, were 3,370 (Gray Rock), 1,950 (Corra), 1,960 (Late Acquisition), and 2,570 (Railroad Bed).

Mean concentrations of copper in remote and rural precipitation ranges were 0.013–1.83 and 0.68–1.5 ppb, respectively, on a volume-weighted basis (Barrie et al. 1987). Although an earlier survey referred to by these investigators yielded much higher values, 0.060 and 5.4 ppb, these were ascribed to sample contamination. The mean concentration of copper in rain reported in an extensive study in southern Ontario, Canada, was 1.57 (0.36 standard deviation) ppb during 1982 (Chan et al. 1986). These concentrations showed little spatial variability and agree with those reported by Barrie et al. (1987). Concentration of copper in cloud water over Olympic Peninsula in Washington State has been measured at  $1.7 \pm 1.6$  µg/L (air-equivalent mean concentration of 0.5 ng/m<sup>3</sup>) (Vong et al. 1997).

Elevated levels of copper in fog water have been observed 3 km downwind from a refuse incinerator in Switzerland (Johnson et al. 1987). High concentrations of copper were associated with low pH. The maximum concentration, 673 ppb, occurred at pH 1.94; levels >127 ppb were associated with pH values <3.6. Copper(II) concentrations in fog water from the central valley of California were 1.7–388 ppb (Miller et al. 1987). The source of the copper was not investigated. High values were recorded just as the fog was dissipating.

The concentration of copper in rain in proximity to a municipal waste incinerator has been found to range from 0.11 to 2.12 µg/L with a mean concentration of 0.87 µg/L. The total mean deposition rate of airborne copper from rain was measured at 4.0 µg/m<sup>2</sup>/day (Feng et al. 2000). However, copper deposition from automobile emissions, as measured by the concentration of copper in snow, did not vary significantly as a function of distance from a roadway (15–150 meters). Mean concentrations of copper in snow (expressed as mg/L [and standard deviations] were measured as; 0.051 (0.073); 0.065 (0.127); 0.034 (0.027); and 0.044 (0.051) at 15, 20, 15, and 150 meters, respectively (Lorganger et al. 1996).

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**Table 6-6. Particle Size Distributions and Total Copper Concentrations in Dust Collected at Four Mine Waste Pump Sites in Butte, Montana<sup>a</sup>**

Site	Particle size ( $\mu\text{m}$ )	Percent in total dust collected	Concentration of copper (ppm, w/w)
Corra	4.7–10	76.6 $\pm$ 4.8	1,550
	1.1–4.7	20.9 $\pm$ 0.63	3,110
	<1.1	1.9 $\pm$ 0.14	4,900
Gray Rock	4.7–10	84.5 $\pm$ 0.93	3,240
	1.1–4.7	13.6 $\pm$ 0.82	4,120
	<1.1	1.9 $\pm$ 0.14	4,370
Railroad Bed	4.7–10	61.5 $\pm$ 1.06	2,580
	1.1–4.7	31.3 $\pm$ 0.96	2,850
	<1.1	7.2 $\pm$ 0.26	1,400
Late Acquisition	4.7–10	70.3 $\pm$ 1.36	1,560
	1.1–4.7	25.0 $\pm$ 1.18	2,730
	<1.1	4.7 $\pm$ 0.44	3,330

<sup>a</sup>Data obtained from Mullins and Norman 1994

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**6.4.2 Water**

Copper is widely distributed in water since it is a naturally occurring element. Copper levels in surface water range from 0.5–1,000 ppb, with a median of 10 ppb; seawater contains <1–5 ppb (Davies and Bennett 1985; Mart and Nurnberg 1984; Page 1981; Perwak et al. 1980; Yeats 1988). The results of several studies in which copper was detected in drinking water, surface water, and groundwater are presented in Table 6-7. The information in Table 6-7 demonstrates that copper concentrations in drinking water can vary widely (#5–10,200 ppb) and can exceed the action limits of 1,300 ppb that have been set for copper in drinking water (EPA 1991). The table also emphasizes the importance of running tap water before using it and the need to control corrosion of piping in water distribution systems.

Copper concentrations in drinking water vary widely as a result of variations in pH, hardness of the water supply, and copper picked up in the water distribution system (Davies and Bennett 1985; Yannoni and Piorkowski 1995). Copper concentrations in drinking water range from a few ppb to 10 ppm. A Canadian national survey of copper and other metals in drinking water was conducted from November 1976 to January 1977 (Meranger et al. 1979). Supplies from 70 municipalities representing 38% of the Canadian population were included in the survey, including 50 derived from river or lake water and 20 derived from groundwater. Unfiltered raw, treated, and distributed drinking waters were analyzed. Whether the water was derived from river, lake, or well water did not significantly affect the copper concentration in the raw water. Only in a few supplies did copper levels in raw water exceed 20 ppb, and only one of these was derived from groundwater. The results in groundwater contrast with those of Page (1981) in New Jersey, in which over 100 wells contained copper levels in excess of 64 ppb. However, that study included groundwater that was a source of drinking water and as well as groundwater that was not. The copper concentration in Canadian treated water was generally . 10 ppb (Meranger et al. 1979). In 20% of the samples, the copper level in distributed water was significantly higher than the treated water; the increase was greater in areas where the water was soft and corrosive, thus enhancing leaching of copper from the distribution system.

Elevated concentrations of copper in drinking water can result as a consequence of leaching processes that occur in water distribution systems. A study of 1,000 water samples from random households in Ohio found that ! 30% contained copper levels >1 ppm (Strain et al. 1984). The highest copper level in the study was 18 ppm. In a study of private water wells in four communities in Nova Scotia, Maessen et al. (1985) found that the concentrations of copper increased in water that remained in the distribution

Table 6-7. Concentrations of Copper in Water

Sample type/ source	Location	Concentration (ppb) Range (mean) [median]	Comments	Reference
Drinking water				
Private wells	Nova Scotia four communities	40–200 130–2,450, 53% of samples >1,000 ppm	at tap, running water at tap, standing water	Maessen et al. 1985
Private wells	New Bedford, Massachusetts	(330)	at tap, running water	Yannoni and Piorkowski 1995
Not specified	Seattle, Washington	(160) (450), 24% of samples >1,000 ppm	running water standing water	Maessen et al. 1985
River water	Canada (National Survey)	#5–530 [#5] #5–100 [#5] #5–220 [20]	raw water treated water distributed water	Meranger et al. 1979
Lake water	Canada (National Survey)	#5–80 [#5] #5–100 [#5] #5–560 [40]	raw water treated water distributed water	Meranger et al. 1979
Well water	Canada (National Survey)	#5–110 [#5] #5–70 [#5] 10–260 [75]	raw water treated water distributed water	Meranger et al. 1979
School drinking water	New Jersey	BD–10,200 <sup>a</sup> BD–7,800 BD–8,500	first draw 10-minute flush mid-day, first draw	Murphy 1993
Groundwater				
Representative sample	New Jersey	[5.0]	1,063 samples, 90 <sup>th</sup> percentile 64.0 ppb, maximum 2,783 ppb, groundwater may or may not be used for drinking water	Page 1981

**Table 6-7. Concentrations of Copper in Water (continued)**

Sample type/ source	Location	Concentration (ppb) Range (mean) [median]	Comments	Reference
Shallow monitoring well	Denver, Colorado	<1–14 [2]	30 monitoring wells, 22 with PVC casings and 8 with metal casings; samples obtained after purging well from 20 minute	Bruce and McMahon 1996
Surface water				
U.S. Geological Survey stations	United States	(4.2) [4.0]	53,862 occurrences	Eckel and Jacob 1988
Representative sample	New Jersey	[3.0]	590 samples, 90 <sup>th</sup> percentile 9.0 ppb, maximum 261 ppb	Page 1981
Surface, marine	East Arctic Ocean	(0.126)	26 locations 0.5–1 m depth	Mart and Nurnberg 1984
Surface, marine	Atlantic Ocean	0.0572–0.0210	20 sites, 2 cruises, 0–1 m depth	Yeats 1988
Pond	Massachusetts	<10–105	Low in summer, high in winter	Kimball 1973
Lakes	Canada	1–8 (2)	Acid sensitive lakes	Reed and Henningson 1984
Lakes	Great Lakes	629–834 (756) 703–1,061 (870) 540–1,098 (830)	Lake Superior Lake Erie Lake Ontario	Nriagu et al. 1996
	Representative samples, nearby to acidic mine drainage	32-1,200 (736)	12 samples taken from streams and ponds near abandoned coal mines in Indiana	Allen et al. 1996
	Representative samples from copper mining areas in Arizona	100–69,000 [1,200]	Samples obtained from the Cerbat Mountains mining area; 15 surface water sites with 14 sites downstream from old tailings and adits	Rösner 1998

<sup>a</sup>BD = below detection limit

## 6. POTENTIAL FOR HUMAN EXPOSURE

system overnight, indicating that copper was mobilized from the distribution system. Whereas the level of copper in running water was generally very low, that in the standing water was variable and exceeded 1.0 ppm in 53% of the homes. Correlation with pH and nitrate, chloride, and manganese concentrations accounted for >99% of the copper picked up from the distribution system. Similar results were reported for U.S. cities (Maessen et al. 1985; Schock and Neff 1988; Strain et al. 1984). In a study in Seattle, Washington, the mean copper concentrations in running and standing water were 0.16 and 0.45 ppm, respectively, and 24% of the standing water samples exceeded 1.0 ppm (Maessen et al. 1985). The difference in copper level between standing and flushed systems became evident at pH 7 and increased with decreasing pH (Strain et al. 1984). Copper levels in school drinking water were found to differ by 3-fold between first draw and 10-minute flush water samples, irrespective of the corrosiveness of the water (Murphy 1993). However, the concentration of copper in both first draw and 10-minute flush samples decreased by approximately 10-fold as the corrosiveness of the water decreased. Increasing pH in water distribution lines has been found to result in an overall decrease in metal concentrations. For example, increasing the pH of water from 7.5 to 8.5 in distribution lines decreased copper concentration by 50% (Yannoni and Piorkowski 1995).

The geometric mean (standard deviation) and median concentration of dissolved copper in surface water based on 53,862 occurrences in EPA's STORET database are 4.2 (2.71) and 4.0 ppb, respectively (Eckel and Jacob 1988). Higher concentrations tend to be found in New England, the western Gulf, and the lower Colorado River (Perwak et al. 1980). An analysis of high concentrations of copper in minor river basins reported in EPA's STORET database in 1978 revealed that sources of copper in the Gila, Coeur D'Alene, and Sacramento River Basins appear to be primarily mining activities, especially abandoned sites (Perwak et al. 1980). The high concentrations were generally observed at localized stations. The low pH of the surface water in these areas was reported to exacerbate the situation. However, in another study concerning lakes sensitive to acid rain, copper values were relatively low (1–8 ppb range, 2 ppb mean) regardless of pH or alkalinity (Reed and Henningson 1984).

Copper concentrations were measured in surface water obtained from sampling sites in the Spearfish Creek, Whitewood Creek, and Bear Butte Creek watersheds. These watersheds are affected by water leaching processes tailings and acid-mine drainage from gold mining operations in the Black Hills of South Dakota. Concentrations of <0.24–28 µg/L were measured in surface water, whereas concentrations in sediments were much higher, ranging from 7.8 to 159 µg/g (May et al. 2001).

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In a survey of sources of copper in storm water, measurements of copper concentrations in storm water samples were taken from various urban locations in Birmingham, Alabama. Copper concentrations were generally low in filtered samples (dissolved copper), ranging between 1.4 and 20 µg/L, but were much higher in unfiltered samples (copper bound to particulate matter) with mean values (in µg/L) of 110 (roof areas), 116 (parking areas), 280 (street runoff), 135 (vehicle service areas), 81 (landscaped areas), 50 (urban creeks), and 43 (detention ponds) (Pitt et al. 1995).

As a result of improvements in controlling discharges from municipal and industrial waste water treatment plants mandated in the Clean Water Act, copper concentrations have been declining in surface waters. For example, median copper concentrations in the Hudson River estuary have fallen 36–56% between the mid-1970s and the mid-1990s (Sañudo-Wilhelmy and Gill 1999).

In a study of representative groundwaters and surface waters throughout New Jersey in which >1,000 wells and 600 surface sites were sampled, the median copper levels in groundwater and surface water were 5.0 and 3.0 ppb, respectively (Page 1981). The respective 90<sup>th</sup> percentile and maximum levels were 64.0 and 2,783.0 ppb for groundwater and 9.0 and 261.0 ppb for surface water. The pattern of contamination in surface water correlates with light hydrocarbons, while that in groundwater correlates with heavy metals. This indicates that the sources of contamination of surface water and groundwater are probably different. The nature of the sites with elevated levels of copper was not indicated. Experimental data demonstrate that leaching of copper is minimal.

The copper concentration in some bodies of water evidently varies with season. In one small pond in Massachusetts, the concentration varied from <10 to 105 ppb (Kimball 1973); copper levels were low from summer to late fall and rose to maximum levels in midwinter. Similar seasonal variations are also noted in the epilimnion of the offshore waters of the Great Lakes (Nriagu et al. 1996). This cycling in copper concentrations is thought to be a response to biological need and uptake of copper during the growing season and its subsequent release from decay of biota.

Copper concentrations in seawater are usually in the 1–5 ppb range (Perwak et al. 1980). Copper levels are lower in the Pacific Ocean than in the Atlantic Ocean and higher near the continental shelf than in the open ocean. Copper concentrations in surface water transected on a cruise from Nova Scotia to the Sargasso sea ranged from 57.2 to 210 parts per trillion (ppt) (Yeats 1988). The mean value in surface water of the eastern Arctic Ocean was 93 ppt (Mart and Nurnberg 1984). In a review by Kennish (1998), concentrations of copper were 0.3–3.8 ppb in estuarine waters and in 0.1–2.5 ppb in coastal waters.

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**6.4.3 Soil and Sediment**

Copper occurs naturally at levels of ~ 50 ppm in the earth's crust, which includes soil and parent rock (Perwak et al. 1980). In the United States, copper concentrations in differing soil types can vary over a large range (1–300 mg/kg, dry weight), but the mean values are relatively similar (14–41 mg/kg, dry weight) as a function of soil type (Table 6-8) and land resource region (Table 6-9). In agriculturally productive soils, copper ranges from 1 to 50 ppm, while in soil derived from mineralized material copper, levels may be much higher (NRC 1977; Perwak et al. 1980). Copper concentrations in soil samples collected throughout the United States yielded a geometric mean of 17–18 ppm (Chen et al. 1999; Fuhrer 1986). Samples were taken at a depth of 8 inches to avoid anthropogenic contamination; 2/3 of the samples contained copper concentrations between 8 and 40 ppm. These copper levels are supported by a review of soil copper concentrations that reported a median concentration of 30 ppm (dry weight) and a range of 2–250 ppm (Davies and Bennett 1985). Copper concentrations in soil may be much higher in the vicinity of a source. Concentrations in the top 5 cm of soil near the boundary of a secondary copper smelter were  $2,480 \pm 585$  ppm (Davies and Bennett 1985). Maximum wetland soil/sediment copper concentrations were 6,912 ppm in the immediate vicinity of a Sudbury, Ontario smelter, but the concentration decreased logarithmically with increasing distance from the smelter (Taylor and Crowder 1983). Results suggest that copper in the soil from the study area was primarily from particulate emissions from the smelter.

In a study in which the copper concentrations of 340 soil samples were presented in terms of land-use types, the average copper concentrations reported were 25 ppm in agricultural land, 50 ppm in suburban/residential land, 100 ppm in mixed industrial/residential land, and 175 ppm in industrial/inner urban areas (Haines 1984). From an analysis of the spatial distribution of the copper, it was concluded that most of the contamination was a result of airborne deposition from industrial sources. Soils from Lemhi, Twin Falls, and the Idaho National Engineering Laboratory in southern Idaho had geometric mean copper concentrations of 13.4–20.4 ppm dry weight (Rope et al. 1988).

The concentration of copper in soils and sediments was assessed as part of the National Water-Quality Assessment Program (Rice 1999). The median concentrations of copper at 541 sites throughout the

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**Table 6-8. Concentration of Copper in Surface Soils of the United States  
(in ppm-Dry Weight [dw], Equivalent to mg/kg-dw)<sup>a</sup>**

Soil	Range	Mean
Sandy soils and lithosols on sandstones	1–70	14
Light loamy soils	3–70	25
Loess and soils on silt deposits	7–100	25
Clay and clay loamy soils	7–70	29
Alluvial soils	5–50	27
Soils over granites and gneisses	7–70	24
Soils over volcanic rocks	10–150	41
Soils over limestones and calcareous rocks	7–70	21
Soils on glacial till and drift	15–50	21
Light desert soils	5–100	24
Silty prairie soils	10–50	20
Chernozems and dark prairie soils	10–70	27
Organic light soils	1–100	15
Forest soils	7–150	17
Various soils	3–300	26

<sup>a</sup>From Breckenridge and Crockett 1995

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**Table 6-9. Geometric Means of Selected Soil Elements and Associated Soil Parameters in U.S. Surface Soils by Land Resource Regions<sup>a</sup>**

Land resource region	mg/kg dry soil
Mineral soils	
Northwestern specialty	34.3
Northwestern wheat	23.2
California subtropical	43.4
Western range and irrigated	26.8
Rocky Mountain	19.1
Northern Great Plains	20.2
Western Great Plains	16.3
Central Great Plains	12.6
Southwest Plateau	10.0
Southwest Prairie	4.9
Northern lake states	15.4
Lake states	18.2
Central feed grains	19.7
East and central farming	8.0
Mississippi Delta	21.1
South Atlantic and Gulf slope	6.3
Northeastern forage	34.0
Northern Atlantic slope	13.5
Atlantic and Gulf coast	7.6
Florida subtropical	31.9
All mineral soils	15.6
Histosols	
Northern lake states	59.6
Lake states	84.7
Northeastern forage	149.0
Florida subtropical	94.3
All histosols	86.9

<sup>a</sup>Source: Holmgren et al. (1993)

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conterminous United States ranged from 5 to 70  $\mu\text{g/g}$  (dry weight). At nonurban indicator sites, the median concentrations ranged from 13 to 47  $\mu\text{g/g}$ . The same study derived an average crustal abundance of copper of 60  $\mu\text{g/g}$ . In the work of Ma et al. (1997), the typical concentration of copper in soils of the United States was determined to be 30 mg/kg, whereas the copper concentration in agricultural surface soils was found to be 18 mg/kg. In Florida surface soils, the geometric mean of copper concentration in all soils was 4.10 mg/kg, with a range of 1.89–10.7 mg/kg with highest levels in ultisol soils (Ma et al. 1997). Chen et al. (1999) reported copper concentrations in Florida soils ranging from 0.1 to 318 mg/kg with a geometric mean of  $2.21 \pm 3.15$  mg/kg (arithmetic mean of  $6.10 \pm 22.1$  mg/kg). These investigators also reported geometric means of 24.0 mg/kg in California soils and 17 mg/kg in U.S. soils.

Sediment is an important sink and reservoir for copper. In pristine areas, sediment generally contains <50 ppm copper; the level can reach several thousand ppm in polluted areas (Harrison and Bishop 1984). The mean copper level in surficial sediment of Penobscot Bay, Maine, was 14.1 ppm (dry weight), while that in estuaries or bays in other New England locations ranged from 4.4 to 57.7 ppm (Larsen et al. 1983b). Levels reflect anthropogenic input as well as the mineral content of the regional bedrock. Copper levels in sediment from 24 sites along the New Jersey coast ranged from <1.0 to 202 ppm, with a mean value of 66 ppm (Renwick and Edenborn 1983). The texture of the sediment varied from 94% clay to 100% sand, and the copper level was correlated negatively with the percentage of sand in the sediment.

Surficial sediment in lakes in the Sudbury region of northeastern Ontario, where several smelters operate, decreased rapidly with increasing distance from the smelters (Bradley and Morris 1986). Three lakes, 10 km from the Sudbury smelters, contained copper concentrations in sediment approaching 2,000 ppm dry weight, over 100 times the concentration in a baseline lake 180 km away.

An analysis of the Coastal Sediment Database (COSED) showed that 75% of coastal waterways had copper concentrations below 42  $\mu\text{g/g}$ ; 2% were above 210  $\mu\text{g/g}$ . These higher concentrations are associated with locations of high ship traffic, industrial activity, and relatively poor water flushing (Daskalakis and O'Connor 1995). In coastal areas receiving persistently high influxes of contaminants, high concentrations of copper have been measured to sediments to depths of 54 cm. Combined sewer outflows can also contribute significantly to the copper content in sediments. For example, mean (arithmetic) copper concentrations of 180, 208, 280, and 284 mg/kg were measured in sediment samples obtained near four sewer outflows in the lower Passaic River, New Jersey (Iannuzzi et al. 1997). In Jamaica Bay, New York, copper concentrations in sediments were 151–406 ppm, with a concentration of 151 ppm in sediment core samples obtained at a depth of 52–54 cm (Bopp et al. 1993). The highest

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concentrations were found in the middle depths (16–44 cm) ranging from 280 to 406 ppm, whereas copper concentrations in surface sediments (0–2 cm) were measured at 208 ppm. The decrease in copper concentration in the surface sediments suggests that efforts to reduce metal contaminants from sewage outflows has been making an impact on the copper concentrations in receiving waters and their sediments.

Copper and its compounds were found at 884 of 1,613 hazardous waste sites on the NPL of highest priority sites for possible remedial action (HazDat 2002). Since copper is found in soil, it should occur at all sites. In past work, data analysis of metal concentrations in soil at hazardous waste sites taken from the 1980–1983 Contract Laboratory Program (CLP) Analytical Results Data Base (CARD) was conducted to ascertain whether elemental concentrations at hazardous waste sites were elevated above that which would normally be expected in soil. Of the 1,307 samples in CARD, 10.5 and 7.3% had copper concentrations exceeding the number normally expected in soil at the 95 and 99% confidence intervals, respectively (Eckel and Langley 1988).

#### **6.4.4 Other Environmental Media**

More recent measurements of copper concentrations in 265 foods measured from 1991 to 1996 and from 1991 to 1999 have been obtained from the FDA Total Diet Study (Capar and Cunningham 2000; FDA 2000). The copper contents of selected foods provided in the most recent FDA Total Diet Study (FDA 2000) are similar to those obtained from the 1982–1984 FDA study; therefore, the daily dietary copper intakes determined in the work of Pennington et al. (1986) are expected to be reliable for estimating current dietary copper intakes. The contribution of food groups to copper intake varies depending on the age group (Pennington and Schoen 1996). For example, animal flesh only contributes to 18% of the copper intake for a 2-year-old child, but contributes to 38% of the copper intake for a 60–65-year-old male. The results of a 1994–1996 Continuing Survey of Food Intakes (CSFII) found that the daily intakes of copper for men and women ages 60 years old are 1.3 and 1.0 mg/day, respectively (Ma and Betts 2000). In a separate study by Ellis et al. (1997), copper intake for male and female African-Americans ages 21–65 years old was determined to be 1.0 mg/day for both sexes.

Daily intakes of copper and other essential minerals were estimated for eight age-sex groups of the United States population as part of the FDA's Total Diet Study (Pennington et al. 1986). By analyzing the mineral content of composite samples of 234 foods obtained in 24 cities from mid-1982 to mid-1984 and by using previously determined daily intakes of each food, the daily mineral intake for the age-sex groups

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was determined. The copper intakes in mg/day of the eight age-sex groups were: 6–11-month-old infant, 0.47; 2-year-old child, 0.58; 14–16-year-old girl, 0.77; 14–16-year-old boy, 1.18; 25–30-year-old woman, 0.93; 25–30-year-old man, 1.24; 60–65-year-old woman, 0.86; and 60–65-year-old man, 1.17. All values were low in terms of the estimated safe and adequate daily dietary intake of this nutrient. The food item with the highest copper level was beef/calf liver (61 ppm).

A baseline value for the copper content of mother's milk was determined by screening literature values. The 28 samples selected had copper concentrations ranging from 197 to 751 ppb and a median of 290 ppb (Iyengar and Woittiez 1988). In a separate study, it was found that the variability was primarily subject-related, but for individuals, the copper concentration in milk declined moderately with the duration of lactation (Vaughan et al. 1979). In a study of 82 healthy, lactating women, the copper concentration in breast milk ranged between 0.8 and 1.1 ppm and remained relatively constant in individual women over the first 7 days postpartum (Arnaud and Favier 1995).

As a part of the National Contaminant Biomonitoring Program of the U.S. Fish and Wildlife Service, eight species of freshwater fish were collected at 112 stations in the United States in 1978–1979 and 1980–1981 (Lowe et al. 1985). The geometric mean concentrations of copper in ppm (wet weight, whole fish) for these two periods were 0.86 and 0.68, respectively; the 85th percentiles were 1.14 and 0.90, respectively, and the ranges were 0.29–38.75 and 0.25–24.10, respectively. The highest concentration, 38.75 and 24.10 ppm, during both collecting periods was in white perch from the Susquehanna River and the second highest concentration, 19.3 ppm, was found in white perch from the Delaware River near Trenton, New Jersey. However, copper concentrations in common carp and white catfish collected from the same station at the same time were 0.76 and 1.35 ppm, respectively.

In bluefin tuna caught in the northwest Atlantic off Newfoundland, the mean copper concentration in muscle tissue has been measured at 1.0 ppm (dry weight) (Hellou et al. 1992a). In cod caught off the coast of Newfoundland, mean copper concentrations of <1.2–1.5 µg/g (dry weight) in muscle and 5–10 ppm (dry weight) in liver have been determined (Hellou et al. 1992b).

Copper residues in muscle of 268 fish specimens were analyzed over a 5-year period in several surface water systems in eastern Tennessee (Blevins and Pancorbo 1986). The mean residue levels in the muscle of different species of fish from nine stations ranged from 0.12–0.86 ppm (wet weight). Maximum levels ranged from 0.14 to 2.2 ppm.

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Concentrations of copper in three species of fish living in storm treatment ponds have been compared to copper concentrations in controls collected from surrounding surface waters near Orlando, Florida (Campbell 1994). In bluegill sunfish collected from storm water ponds, the mean whole body copper concentrations were 6.37 and 2.08 mg/kg wet weight, respectively, and were significantly higher than the mean concentrations of copper in controls, 0.879 and 1.07 mg/kg wet weight, respectively. However, in largemouth bass, the mean copper concentrations in fish collected from storm water ponds and controls did not significantly differ, with values of 3.81 and 4.71 mg/kg wet weight, respectively.

Respective mean and median copper concentrations of 127 samples of fish from Chesapeake Bay and its tributaries were 1.66 and 0.36 ppm in 1978, and 1.85 and 0.61 ppm in 1979 (Eisenberg and Topping 1986). Copper levels were increased in the livers and to a lesser degree, the gonads, compared with the flesh. The copper content of muscle tissue of several species of fish collected from metal-contaminated lakes near Sudbury, Ontario, ranged from 0.5 to 1.4 ppm (dry weight). No major pattern in variation was evident among species or among the study lakes (Bradley and Morris 1986). The copper concentration in the livers, however, ranged from 5 to 185 ppm (dry weight) and differed significantly among species and among lakes. Unlike muscle tissue, liver tissue is a good indicator of copper availability, although the data indicate that there are other factor(s) that influence the availability and bioaccumulation of copper in these fish.

The copper concentrations in the liver of lake trout and grayling taken from Arctic fresh water lakes did not correlate well with the concentrations of copper in the sediments of these lakes (Allen-Gil et al. 1997). Lake trout were found to have higher burdens of copper than grayling, and the concentrations of copper in trout varied considerably depending on the lake from which they were collected. The species and site differences in copper concentrations have been attributed to differences in dietary patterns, (grayling consume mainly insects, whereas trout consume a mix of snails, insects, and small fish) and time spent at various depths of the water column.

The concentrations of copper in the soft tissue in mussels and oysters collected as part of the U.S. Mussel Watch Program in 1976–1978 were 4–10 ppm (dry weight) for mussels and 25–600 ppm for oysters (Goldberg 1986). Copper concentrations in mussels collected from 11 sites near Monterey Bay, California, were 4.63–8.93 ppm (dry weight) (Martin and Castle 1984). Perwak et al. (1980) reported similar results for mussels (3.9–8.5 ppm) and clams (8.4–171 ppm). Recent measurements of copper concentrations in zebra and quagga mussels taken from Lakes Erie and Ontario in 1997 ranged from between 21 to 41 ppm (dry weight) (Rutzke et al. 2000). In the National Oceanic and Atmospheric

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Administration (NOAA) Mussel Watch Project, copper concentrations were quantified in mollusks from 113 sites around the United States in 1993 and compared to copper concentrations measured in mollusks taken from the same site in the EPA2 Mussel Watch Program, 1976–1978 (Lauenstein and Daskalakis 1998). The results of the comparison indicate that the decreasing and increasing trends in copper concentrations in mollusks were approximately equal among the sites except in California, where increasing trends were noted at five sites.

Although the concentrations of copper in plants vary widely, they usually range from 1 to 50 ppm (dry weight) (Davies and Bennett 1985; Perwak et al. 1980). Concentration ratios of copper in plants relative to soil (concentration factors or CF) demonstrate that copper uptake and demand differs significantly between plants. For example, CF values have been found to vary from 0.02 (onion), 0.13 (celery), 0.21 (lettuce), and 0.30 (potato) to 2 (grapes), 4.5 (alfalfa), and 6.8 (grass) (Pinochet et al. 1999). Concentration factors in rice were found to vary among soil types (0.59–3.58) with copper concentrations in rice ranging from 1.7 to 5.1  $\mu\text{g/g}$  (Herawati et al. 2000). Copper concentrations in the rice grain have been found to increase significantly from 1.4 to 15.5  $\mu\text{g/g}$  when copper concentrations in waste water irrigated soils increased from 17.0 mg/kg (wet weight) to 101.2 mg/kg (wet weight) (Cao and Hu 2000).

The FDA Total Diet Survey has provided copper concentration in various foods, example of which are given in Table 6-10 (FDA 2001). For copper concentrations measured in the edible tissues of livestock and poultry, the highest mean concentrations (ppm) were found in liver (cow 43.7; lamb 89.8; chicken 4.60; turkey 7.14), followed by kidney (cow 8.15; lamb 5.39; chicken 3.07; turkey 3.68), and muscle (cow 1.41; lamb 1.47; chicken 0.67; turkey 0.83) (Coleman et al. 1992).

Studies of copper in human tissues suggest that copper content in a 70 kg adult range from 50–70 mg (Davies and Bennett 1985). Wise and Zeisler (1984) reported an average copper concentration of 10 ppm in the human liver in 36 samples. Despite the wide variation in copper concentrations in the

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**Table 6-10. Copper Content of Selected Foods (mg/kg)<sup>a</sup>**

Food description	Mean	S.D.	Food description	Mean	S.D.
<b>Breads</b>			green pepper, raw	0.7	0.3
bagel, plain	1.3	0.2	iceberg lettuce, raw	0.2	0.2
cracked wheat bread	1.8	0.2	lima beans, immature, frozen,	1.5	0.2
English muffin, plain, toasted	1.3	0.1	mixed vegetables, frozen,	0.6	0.2
graham crackers	1.5	0.3	mushrooms, raw	2.4	0.6
rye bread	1.5	0.2	okra, fresh/frozen, boiled	0.8	0.3
saltine crackers	1.4	0.1	onion, mature, raw	0.4	0.1
white bread	1.1	0.2	peas, mature, dry, boiled	2.3	0.3
white roll	1.3	0.2	spinach, fresh/frozen, boiled	0.8	0.3
whole wheat bread	2.3	0.3	summer squash, fresh/frozen,	0.5	0.1
<b>Cereal, rice, and pasta</b>			sweet potato, fresh, baked	1.4	0.4
corn flakes	0.5	0.1	tomato, red, raw	0.5	0.2
crisped rice cereal	2.0	0.2	tomato sauce, plain, bottled	1.2	0.4
egg noodles, boiled	1.0	0.2	tomato, stewed, canned	0.7	0.2
granola cereal	3.0	0.4	turnip, fresh/frozen, boiled	0	0.1
macaroni, boiled	0.9	0.1	white potato, baked with skin	1.0	0.4
oatmeal, quick (1–3 minutes),	0.7	0.1	white potato, boiled without	0.6	0.2
oatring cereal	3.3	0.4	winter squash, fresh/frozen,	0.6	0.2
raisin bran cereal	4.4	0.4	<b>Fruits</b>		
shredded wheat cereal	3.7	0.5	apple, red, raw	0.2	0.2
wheat cereal, farina, quick	0.3	0.3	applesauce, bottled	0.2	0.1
white rice, cooked	0.7	0.1	apricot, raw	0.8	0.3
<b>Vegetables</b>			avocado, raw	2.2	0.6
asparagus, fresh/frozen,	1.0	0.2	banana, raw	1.1	0.2
beets, fresh/frozen, boiled	0.7	0.2	cantaloupe, raw	0.3	0.1
black olives	1.4	0.4	fruit cocktail, canned in heavy	0.5	0.1
broccoli, fresh/frozen, boiled	0.2	0.1	grapefruit, raw	0.3	0.1
Brussels sprouts, fresh/frozen,	0.4	0.1	grapes, red/green, seedless,	1.1	0.6
cabbage, fresh, boiled	0	0	orange, raw	0.4	0.1
carrot, fresh, boiled	0.3	0.2	peach, canned in light/medium	0.3	0.2
cauliflower, fresh/frozen,	0	0	peach, raw	0.7	0.2
celery	0	0.1	pear, canned in light syrup	0.4	0.1
collards, fresh/frozen, boiled	0.5	0.4	pear, raw	0.8	0.1
corn, fresh/frozen, boiled	0.3	0.2	pineapple, canned in juice	0.5	0.1
cream style corn, canned	0.1	0.2	plums, raw	0.6	0.1
cucumber, raw	0.2	0.2	prunes, dried	2.9	0.3
eggplant, fresh, boiled	0.5	0.2	raisins, dried	3.3	0.4
green beans, fresh/frozen,	0.5	0.3	strawberries, raw	0.5	0.3
green peas, fresh/frozen,	1.0	0.2	watermelon, raw	00.4	0.1

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**Table 6-10. Copper Content of Selected Foods (mg/kg)<sup>a</sup> (continued)**

Food description	Mean	S.D.	Food description	Mean	S.D.
<b>Fruit juices</b>			pork roast, baked	0.8	0.1
apple juice, bottled	0	0.1	pork sausage, pan-cooked	0.8	0.1
grape juice, bottled	0	0.1	quarter-pound hamburger on	0.9	0.1
grapefruit juice, from frozen	0.3	0.1	salami, sliced	1.0	0.2
orange juice, from frozen	0.3	0.1	salmon, steaks or filets, fresh	0.5	0.1
pineapple juice from frozen	0.4	0.1	shrimp, boiled	2.3	0.6
prune juice	0.1	0.1	tuna, canned in oil	0.5	0.1
tomato juice, bottle	0.6	0.1	turkey breast, roasted	0.4	0.1
			veal cutlet, pan-cooked	1.0	0.3
<b>Dairy products</b>			<b>Legumes, nuts, and nut products</b>		
American, processed cheese	0.1	0.2	kidney beans, dry, boiled	2.7	0.5
chedder cheese	0.3	0.2	mixed nuts, no peanuts, dry	15.5	2.6
chocolate milk, fluid	0.3	0.2	peanut butter, smooth	5.2	0.6
cottage cheese, 4% milkfat	0	0	peanuts, dry roasted	5.8	0.6
cream cheese	0	0	pinto beans, dry, boiled	2.4	0.2
eggs, boiled/fried	0.6	0.1	pork and beans, canned	1.8	0.2
eggs, scrambled	0.5	0.1	<b>Fats, oils, condiments, snacks, and sweets</b>		
half & half	0	0	butter, regular (salted)	0	0
lowfat (2%) milk, fluid	0	0	corn chips	1.0	0.2
skim milk	0	0	fruit flavor sherbert	0	0.1
sour cream	0	0	gelatin dessert, any flavor	0	0
Swiss cheese	0.4	0.4	honey	0	0
whole milk	0	0	jelly, any flavor	0	0.1
<b>Meat, poultry, and seafood</b>			margarine, stick, regular	0	0
beef chuck roast, baked	1.0	0.1	mayonaise, regular, bottled	0	0
beef steak, loin, pan-cooked	1.0	0.2	olive/safflower oil	0	0
bologna, sliced	0.4	0.2	popcorn, popped in oil	1.7	0.4
chicken breast, roasted	0.3	0.1	potato chips	2.8	0.8
chicken, fried (breast, leg, and	0.7	0.1	pretzels, hard, salted, any	1.6	0.2
frankfurters, beef, boiled	0.4	0.1	vanilla ice cream	0.06	0.24
ground beef, pan-cooked	0.8	0.1	white sugar, granulated	0	0
haddock, pan-cooked	0.06	0.13	<b>Beverages</b>		
ham, baked	0.6	0.2	coffee, from ground	0	0
ham luncheon meat, sliced	0.5	0.1	cola carbonated beverage	0	0
lamb chop, pan-cooked	1.4	0.2	tea, from tea bag	0	0
liver, beef, fried	123	57			
pork bacon, pan-cooked	1.2	0.4			
pork chop, pan-cooked	0.8	0.2			

<sup>a</sup>Data excerpted from the U.S. FDA Total Diet Study (2001).  
S.D. = Standard Deviation

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environment, the copper concentration in the liver only varied by a factor of 2–3.5. Copper concentrations in human tissues are given in Table 6-11 (Georgopoulos et al. 2001). The concentration of copper in blood is not expected to be predictive of the total body burden of copper; Saltzman et al. (1990) have found that the correlation between copper concentrations measured in blood and total body burden was poor ( $r=0.54$ ).

The mean copper content of cigarette tobacco was 24.7 ppm, with a standard deviation of 10.8 ppm (Mussalo-Rauhamaa et al. 1986). However, only 0.2% of this copper passes into mainstream smoke. This translates to a daily exposure of approximately 1 µg of copper in a pack of 20 cigarettes.

In an EPA-sponsored study conducted to determine the metal concentration in sewage sludge (Feiler et al. 1980), copper concentrations in primary sludge at seven POTWs were reported to be 3.0–77.4 ppm, with a median concentration of 20.5 ppm. The plant with the highest copper concentrations received wastes from plating industries, foundries, and coking plants. In a comprehensive survey of heavy metals in sewage sludge, 30 sludges from 23 American cities were analyzed (Mumma et al. 1984). The copper concentration in the sludges ranged from 126 to 7,729 ppm (dry weight), with a median value of 991 ppm. In the EPA National Sewage Sludge Survey, the mean concentration of copper in sewage sludge was 741 mg/kg (dry weight) (He et al. 1995). Gutenmann et al. (1994) report similar concentrations (217–793 ppm, dry weight) in sewage sludge obtained from 16 major cities in the United States. The proposed limit for copper in sludge spread on agricultural land is 1,000 ppm (Mumma et al. 1984). For comparison, the concentration of copper in cow's manure is . 5 ppm (Mumma et al. 1984).

In municipal solid waste compost obtained from nine sites in the United States, a mean copper concentration of 281 mg/kg (dry weight) was obtained with range of 36.4–424 mg/kg (He et al. 1995). Lisk et al. (1992) reported copper concentrations in composts formed from yard waste, ranging from 22.7 to 327 ppm, from sewage sludge ranging from 432 to 1,019 ppm, and from municipal solid waste ranging from 191 to 1,143 ppm.

Copper concentrations in waste from the combustion of municipal solid waste and other combustion processes have been reported. Copper in incinerator bottom ash and fly ash has been measured at mean concentrations of 1,700 and 1,000 mg/kg, respectively (Goldin et al. 1992). Buchholz and Landberger (1995) report concentrations of copper of 390–530 µg/g in fly ash, 1,560–2,110 µg/g in bottom ash, and

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**Table 6-11. Copper Content of Human Tissues and Body Fluids**

Tissue	Mean content ( $\mu\text{g/g}$ dry weight)	
	Normal	Wilson's disease
Adrenal	7.4	17.6
Aorta	6.7	—
Bone	4.2	—
Brain	—	—
Caudate nucleus	—	212
Cerebellum	—	261
Frontal lobe cortex	—	118
Globus pallidus	—	255
Putamen	—	314
Cornea	—	92.9
Erythrocytes (per 100 ml packed red blood cells)	23.1	—
Hair	89.1	—
Heart	16.5	12.7
Kidney	14.9	96.2
Leukocytes (per 10 <sup>9</sup> cells)	0.9	—
Liver	25.5	584
Lung	9.5	15.5
Muscle	5.4	25.9
Nail	18.1	—
Ovary	8.1	5.2
Pancreas	7.4	4.2
Placenta	13.5	—
Prostate	6.5	—
Skin	2	5.2
Spleen	6.8	5.6
Stomach and intestines	12.6	22.9
Thymus	6.7	—

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**Table 6-11. Copper Content of Human Tissues and Body Fluids (continued)**

Tissue	Mean content ( $\mu\text{g/g}$ dry weight)	
	Normal	Wilson's disease
Thyroid	6.1	—
Uterus	8.4	—
Aqueous humor	12.4	—
Bile (common duct)	1,050	173
Cerebrospinal fluid	27.8	—
Gastric juice	28.1	—
Pancreatic juice	28.4	—
Plasma, Wilson's disease		—
Saliva	50	—
Serum		
Female	120	—
Male	109	—
Newborn	36	—
Sweat		
Female	148	—
Male	55	—
Tissue		
Synovial fluid	21	—
Urine (24-hour)	18	—

Source: Georgopoulos et al. (2001); Scheinberg (1979); Sternlieb and Scheinberg (1977)

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1,140–1,540 µg/g in combined ash. In sewage sludge incineration process steams, copper concentrations were 4,561 mg/kg in sludge cake, 3,465 mg/kg in bottom ash, 3,707 mg/kg in cyclone ash, 3,684 mg/kg in scrubber particulate matter, and 6,666 mg/kg in stach particulate matter (Balogh 1996). In fossil fuel wastes, copper concentrations of 33–2,200 mg/kg in fly ash, 4–930 mg/kg in bottom ash, 6–340 mg/kg in flue gas desulfurization sludge, 10–130,000 mg/kg oil ash, and 2–190 mg/kg in coal have been obtained (Eary et al. 1990).

Agricultural sources of copper contamination in soils has been summarized by EPA (1995) and are shown in Table 6-12. Concentrations of copper in fertilizers, soil amendments, and other agricultural materials have been measured by Raven and Loeppert (1997). The materials and mean concentrations: urea (<0.6 µg/g), ammonium nitrate (<0.6 µg/g), ammonium sulfate (<0.6 µg/g), ammonium phosphate (<2–41.8 µg/g), potassium chloride (<2–3.5 µg/g), potassium-magnesium-sulfate (1.4–5 µg/g), North Carolina rock phosphate (9.6 µg/g), calcite (2.3 µg/g), corn leaves (9.4 µg/g), manure (17.5 µg/g), and austinite (300 µg/g).

### 6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Due to the ubiquitousness of copper in the environment and the general occurrence of copper in airborne particulates, exposure to copper through inhalation is commonplace. Estimates of atmospheric copper concentrations from representative source categories yielded a maximum annual concentration of 30 µg/m<sup>3</sup> (EPA 1987a). If a person is assumed to inhale 20 m<sup>3</sup> of air/day, this would amount to an average daily intake of 600 µg of copper. For the reported range of annual atmospheric copper concentrations, 5–200 ng/m<sup>3</sup> (EPA 1987a), the average daily intake by inhalation, would range from 0.1–4.0 µg. At the maximum reported ambient air concentration, 100 µg/m<sup>3</sup> for a 24-hour period at a location within one-half mile of a major source (EPA 1987a), the average daily intake would rise to 2,000 µg. These estimates assume that all of the copper is attached to particles of inhalable size, which is usually not the case. The average daily dietary intake of copper from food is <2 mg/day. Assuming a median copper concentration in drinking water of 75 µg/L, the average daily copper exposure from consumption of 2 L of water per day is 0.15 mg; however, many people may have high levels of copper in their tap water from the water distribution system. If the system is not permitted to flush out, average intakes from water may be >2 mg/day. It is less likely that high dermal exposures will result from bathing in this tap water because the distribution system will flush itself out as the water is drawn. The

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**Table 6-12. Agricultural Sources of Copper Contamination in Soils<sup>a</sup>**

Source	Concentration (ppm dry weight) <sup>b</sup>
Sewage sludges	50–3,300
Phosphate fertilizers	1–300
Limestones	2–125
Nitrogen fertilizers	<1–15
Manure	2–60
Pesticides (percent)	12–50

<sup>a</sup>From EPA 1995<sup>b</sup>Equivalent to mg/kg-dry weight

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total exposure of copper for the average person from all sources (e.g., air, drinking water, and food) is estimated to be 2.75 mg/day.

A National Occupational Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983 estimated that potentially 505,982 workers, including 42,557 women, were occupationally exposed to copper in the United States (NIOSH 1988). The NOES estimate is provisional because all of the data for trade name products that may contain copper have not been analyzed. Of the potential exposures, 1,073 are to pure copper, while in the other cases, the molecular form of copper was unspecified. Additionally, according to the NOES, 125,045 workers, including 38,075 women, were potentially exposed to copper sulfate (NIOSH 1988). The NOES was based on field surveys of 4,490 facilities and was designed as a nationwide survey based on a statistical sample of virtually all workplace environments in the United States where eight or more persons are employed in all standard industrial codes (SIC) except mining and agriculture. The exclusion of mining and agriculture is significant for estimating exposure to copper since there is a high potential for exposure in these industries. Current occupational exposure limits for copper fume are 0.2 and 1 mg/m<sup>3</sup> for dust and mists (Frazier and Hage 1998).

## 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 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).

Exposures of children to copper are not expected to be very different from those in the general population with respect to inhalation. However, exposure of copper through oral routes may differ, due to differences in the consumption of various food groups between children and adults and ingestion of dust and soils. The dietary copper intake for infants who receive the major portion of their nutritional

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requirements from breast milk is likely to be different from infants whose nutritional needs are either supplemented or entirely received through the consumption of formula. From the work of Pennington et al. (1986), the copper intake for a 6- to 11-month-old infant and a 2-year-old child are estimated to be 0.47 and 0.58 mg/day, values which are lower than the adult intake of 1 mg/day. However, little information is available on estimates of copper intake from inhalation and other oral routes for children in the United States. However, one study has provided estimated inhalation and ingestion exposures of copper for children in India (Raghunath et al. 1997). In this work, concentrations of copper in particulates in air were measured at 0.01–0.26  $\mu\text{g}/\text{m}^3$ . Based on these measurements, estimated inhalation exposures of children to copper were calculated to be 0.1–3.2  $\mu\text{g}/\text{day}$ . In this same work, exposures to copper through ingestion were estimated to be between 684–1,732  $\mu\text{g}/\text{day}$ .

Exposures of children to copper are likely to increase in areas where copper concentrations in air are expected to be high, such as mining sites, waste dump sites, smelters, and foundries. For example, copper burdens in children living near a lead smelter, as measured by copper concentration in teeth, increased with decreasing distance from the smelter (Blanuša et al. 1990). Children are also at risk for increased copper intake through consumption of drinking water where leaching of copper from the distribution system has occurred (Murphy 1993; Yannoni and Piorkowski 1995). This route of copper exposure can be minimized through the flushing of drinking water supply lines or increasing the pH of the water in the distribution system.

### 6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In discussing exposure to copper, the important question is whether individuals are exposed to readily available copper, which in general, means free (hydrated) Cu(II), and perhaps some weakly complexed or adsorbed forms of copper. The available data indicate that copper in natural water, sediment, and soil is in a bound form. Even so, the free form of copper can be readily obtained from ingested materials, for example a child's sampling of soil, after exposure to the low pHs encountered in the stomach. Potential for high exposure of the general population to copper may exist where people consume large amounts of tap water that has picked up copper from the distribution system, or already has a high copper background due to natural or anthropogenic activities (e.g., close proximity to mining activities or mine drainage). Leaching of copper from water distribution systems is likely to occur where the water is soft and is not allowed to run and flush out the system. In such cases, the concentration of copper frequently exceeds 1 ppm and a large fraction of the copper may be free cupric ion, and exposure will result by ingestion and dermal contact. A less likely situation where exposure to high levels of free Cu(II) may occur is from

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swimming in water that has been recently treated with a copper-containing algicide. Soluble cupric salts are used extensively in agriculture and in water treatment. Workers engaged in the formulation and application of these chemicals and industrial workers, such as those in the plating industry, may come into dermal contact with these copper-containing chemicals.

Based on the available data, people living close to NPL sites may be at greater risk for exposure to copper than the general population. This exposure can occur through particulates that have been blown offsite from NPL sites, ingestion of water from private wells which are in close proximity to NPL sites, ingestion of contaminated soil, or uptake of copper into fruits and vegetables raised in gardens of residents living near NPL sites.

People living near copper smelters and refineries and workers in these and other industries may be exposed to high levels of copper in dust by inhalation and ingestion. In some industries, workers may be exposed to fumes or very fine dust that may be more hazardous than general dust.

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

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.

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**6.8.1 Identification of Data Needs**

**Physical and Chemical Properties.** The available data on the physical and chemical properties of copper and copper sulfate are generally sufficient for estimating their environmental fate. That no numerical value is listed for the water solubility of copper in Table 4-3 is of no special significance. For inorganic salts, the solubility product coupled with stability constants for the ionic species in solution are the factors determining how much of a compound goes into solution; the solubility in terms of the number of milligrams of the parent compound in solution, as used for organic compounds, is not meaningful. The important solubility products and stability constants for copper that are required for determining the copper species in natural water and their concentrations are known (Schnoor et al. 1987; Town and Filella 2000). Although no  $K_{oc}$  values are listed, copper binds very strongly to organic matter, and values for the binding constants and solubility products to humic acids are available (Schnoor et al. 1987). Similarly, there are binding constants and solubility products for other species that bind or coprecipitate with copper, such as clay minerals and iron and manganese oxides (Schnoor et al. 1987). Binding constants for copper in specific natural waters are also available (Town and Filella 2000). Other physical and chemical properties in Table 4-3 for which there is no data are generally negligible (e.g., Henry's law constant, vapor pressure) or not well defined for copper.

In general, experimental confirmation is required for predicting copper's fate in the environment. The factors which determine the copper species present or the material to which copper may be bound and the strength of the binding are site specific. If the level of detail requires knowledge of, for example, the percentage of copper associated with iron oxides or that which is easily exchangeable, the experimental confirmation is necessary.

**Production, Import/Export, Use, Release, and Disposal.** In the absence of information on the number of, information on the production, use, release, and disposal of copper is used for evaluating the potential for exposure of people to copper who live or work near waste sites and other sources. Copper exposure is widespread, but much of this exposure is to generally benign forms, such as metallic copper. The information available often does not distinguish between these forms and those of greater toxicological significance.

Information on the production, use, release, and disposal of copper and copper sulfate is generally available. The two chemicals account for most of the copper used. This information is tabulated by the U.S. Geological Survey every year in the Minerals Yearbook, and future trends in production and use are

## 6. POTENTIAL FOR HUMAN EXPOSURE

available. Such information is not available for other copper compounds. We also know the major uses of copper and whether these uses occur in the home, workplace, or environment.

According to the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRTKA), (§313), (Pub. L. 99-499, Title III, §313), industries are required to submit release information to the EPA. The TRI contains release information for copper and copper compounds and is updated yearly.

For disposal, industrial waste copper is generally either recycled or landfilled. Data on secondary copper production (i.e., copper produced from scrap) is compiled by the U.S. Geological Survey. Effluent and disposal regulations for copper and its compounds are listed in the Clean Water Act and the Resource Conservation and Recovery Act (RCRA).

**Environmental Fate.** Information on how copper and its compounds partition in the environment (i.e., to soil and sediment), and the type of transformations that occur in different media, is available. We also have data concerning its transport in the environment. Although information on the fate of copper in air, water, and soil is available, the fate of copper is both species- and site- specific. Information concerning the forms of copper (i.e., specific compound, to what it is bound or complexed, or, in the case of air, the particle size) or the lability of the copper in particular media is available from only a few studies. These are sufficient to understand many contributors to the fate of copper and its compounds, but are not as comprehensive as one might like. In addition, studies of how fate data are directly relevant to human exposures, especially in regards to projecting copper toxicity in children is inadequate.

**Bioavailability from Environmental Media.** Copper is found in food, water, ambient air, and soil. The bioavailability of copper from food and water has been investigated in animals and humans. No information on the availability of copper from air was located. Copper in air originating from smelter sites is predominantly associated with sulfur, presumably as the sulfate. Copper dust from soil or around mining and smelter sites may be in a mineral form or as silicates. No information was located on the availability of copper in air. Copper in the soil is often bound to organic molecules; therefore, the bioavailability of the copper from soil cannot be assessed based on bioavailability information from drinking water or food studies. Studies on the bioavailability of copper from soil and ambient air would be useful in assessing potential toxicity to people living near a hazardous waste site.

The form and lability of copper in the environment is known in only a few site-specific cases. None of these cases include hazardous waste sites. More information on the forms of copper found at industrial

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sites and hazardous waste sites would be useful, especially since data from the Hazardous Substances Database Bank (HSDB) indicate that concentrations of copper as high as 182,000 ppm in soil and 14,000 ppm in sediments have been measured offsite of listed NPL sites (HazDat 2002). Monitoring groundwater near industries that use highly acid, copper-containing solutions, such as electroplating, electrowinning, and ore leaching industries, is important with respect to presenting highly mobile and highly bioavailable copper to human risk populations.

**Food Chain Bioaccumulation.** Because copper occurs in different forms in soil and water, the bioaccumulation of copper is expected to vary according to site and species. Data are generally available on the bioconcentration of copper in aquatic organisms, plants, and animals, as well as biomagnification in the food chain. This information is useful in assessing the potential for exposure from ingesting food originating from contaminated areas.

**Exposure Levels in Environmental Media.** Data are generally available regarding the concentrations of copper in environmental media, including the concentration of copper in soil at some hazardous waste sites. Since copper is naturally present in soil, statistical techniques can be used to determine whether the copper found at these sites is elevated above normal levels. Monitoring data are reasonably current. Human intake of copper from food, water, and air can be estimated.

**Exposure Levels in Humans.** Reasonably current data report levels of copper in human tissue and human milk. Although there is an increasing battery of information becoming available that describes copper concentrations in individuals exposed within specific work settings (for example, Gerhardsson et al. 1993; Saltzman et al. 1990), none of these studies address specific U.S. populations living around hazardous waste sites. There are quantitative data relating occupation, level and route of exposure, or the form of copper to which people are exposed. There is some limited information correlating the copper concentration and form to levels in the body in general populations; however, information is needed for occupational and at-risk populations.

**Exposures of Children.** Reasonably current data report levels of copper intake in infants and children. Information on copper intake for infants from human milk is also available. Exposure of children to copper in drinking water has been assessed and methods to decrease this exposure have been identified. However, only limited information on inhalation and other oral routes is available. Some information on exposure of children to copper near mining, smelting, refining, manufacture facilities, waste sites, and other hazardous sites is available, but not for U.S. populations. This information is

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needed to better estimate exposures of children in U.S. populations living near these facilities and sites. The use of copper concentrations in toenails and hair has been investigated as a surrogate measure of copper exposure in children and adults, and more research into testing the use of these surrogates is underway.

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

**Exposure Registries.** No exposure registries for copper and its compounds were located. No subregistry has currently been established for these chemicals. They will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to these chemicals.

### 6.8.2 Ongoing Studies

Ongoing studies of copper in soils, sediments, and aquifers have been identified and are listed in Table 6-13. Also included in Table 6-13 are ongoing investigations of human exposures to copper.

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**Table 6-13. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Copper<sup>a</sup>**

Investigator	Affiliation	Research Description	Sponsor
Barnhisel, RI; Karathanasis, AD; Smith, BR	University of Kentucky; Clemson University	Evaluate the capacity of colloid dispersion models to predict water-dispersible colloid content based on quantifiable mineralogical properties of southern regional soils. Determine the nature of contaminant (e.g., copper)-mineral associations in selected soils as influenced by mineralogy and pedogenic properties and processes.	Hatch
Bleam, WF; Helme, PA	University of Wisconsin at Madison	Investigation of how humic substances in soil bind trace metals. Specific objectives include determining whether nitrogen amine ligands dominate $\text{Co}^{+2}$ , $\text{Ni}^{+2}$ , and $\text{Cu}^{+2}$ complexes at metal:N ratios in the range of 0.2–5.0.	NRI comp. grant
Chaney, RL	Beltsville ARC, Beltsville, Maryland	Comparison of the phytoavailability of Cd, Zn, and Cu in unamended soils versus long-term biosolids amended at equivalent pH to characterize changes in the adsorption equilibria of the paired soils. Evaluation of how changes in Fe and Mn oxides or humics content affect metal uptake.	USDA In-house
Chaney, RL; Daniels, WL	Virginia Polytechnic Institute	Comparison of the phytoavailability of Cd, Zn, and Cu in unamended soils versus long-term biosolids amended at equivalent pH to characterize changes in the adsorption equilibria of the paired soils as a function of the properties of the biosolids and soils. Evaluation of how changes in Fe and Mn oxides or humics content affect metal uptake.	USDA
Eick, MJ	Virginia Polytechnic Institute	Determine the kinetics and mechanisms of orthophosphate and trace elements (Cu, Pd, Cd, and Co) adsorption/desorption reactions on mineral and organic surfaces using a pressure jump relaxation spectrometer.	Hatch
Guo, MG; Tyzbir, R	University of Vermont	The objective is to determine the effective solubility of inorganic versus organic salts of Zn, Fe, and Cu in infant formula and how antioxidants influence the solubility of minerals in formula.	Hatch
Hesterberg, DL	North Carolina State University	Ascertain the nature of heavy metal binding to clay-organic systems and determine the significance of metal sulfides and other stable chemical species for reducing the mobility and bioavailability of metals in soils.	Hatch

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**Table 6-13. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Copper<sup>a</sup> (continued)**

Investigator	Affiliation	Research Description	Sponsor
Louma, SN	Water Resources Division, USGS	Investigate the partitioning of trace metals in sediments and how the partitioning is controlled. Geochemical partitioning, metal uptake into aquatic organisms, and the effects of the metals on these organisms will be examined.	USGS In-house
Morgan, DL	NIEHS	Investigate the absorption, distribution, and pulmonary toxicity of copper-indium diselenide and other novel chemicals used in the semiconductor and photovoltaic industries.	NIEHS Intra-mural
Parker, DR	University of California at Riverside	Objectives are to reexamine the Free Ion Activity Model (FIAM), which describes trace-metal toxicities in crop plants based on the chemical activity of the free metal ion in soil solution.	NRI comp. grant
Simon, NS	Water Resources Division, USGS	Determine the speciation of dissolved, free, inorganic, and organic complexed metals and how inorganic-organic reactions by which metals are retained in, or mobilized from, influence the distribution and partitioning of metals between solution and solid phases in sediments.	USGS
Sparks, DL; Ford, RG	University of Delaware	Determine the sorption-desorption kinetics of Ni, Cu, and Zn in model soils and examine the effect of Al-bearing clay minerals, iron oxides, and organic matter on the formation of mixed metal-Al precipitates.	NRI comp. grant
Strawn, DG	University of Idaho	Investigate Cu and Pd sorption mechanisms on distinct clay mineral surfaces under various equilibrium conditions.	Hatch
Thompson, ML	Iowa State University	Ascertain the binding nature and capacity of copper and Pb with humic components in aquifers and predict transport of these metals in aquifers using nonequilibrium models.	NRI comp. grant
Thompson, ML et al.	Iowa State University	Determine the mineralogical and microenvironmental contexts of Pd, Ni, Cu, and Zn in the solid and liquid phases of metal-contaminated soils.	Hatch

## 6. POTENTIAL FOR HUMAN EXPOSURE

**Table 6-13. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Copper<sup>a</sup> (continued)**

Investigator	Affiliation	Research Description	Sponsor
Zelazny, LW	Virginia Polytechnic Institute	Determine the quantity and chemical forms of P, Cu, and Zn in manure before and after application to soil and ascertain the bioavailability of these metals to plants.	Hatch

<sup>a</sup>CRIS 2002; FEDRIP 2002

ARC = Agricultural Research Center; NIEHS = National Institute of Environmental Health Sciences; NRI = National Research Institute; USDA = U.S. Department of Agriculture; USGS = U.S. Geological Survey