

6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

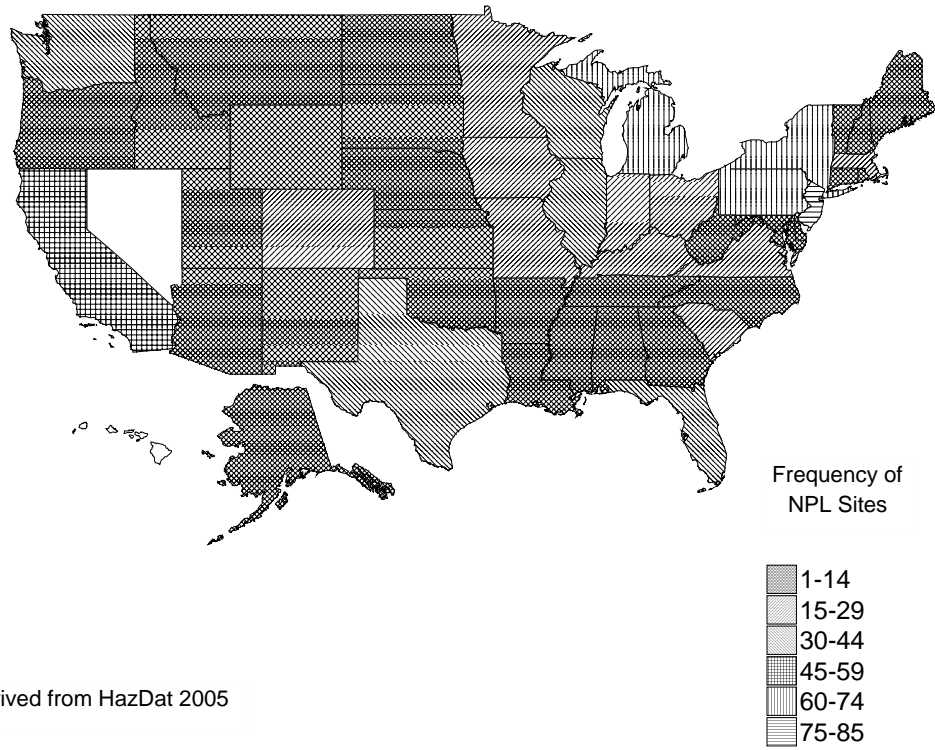
Nickel has been identified in at least 872 of the 1,662 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2005). However, the number of sites evaluated for nickel is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, 862 are located within the United States, 6 are located in the Commonwealth of Puerto Rico, and 4 are located in the Territory of Guam (the Commonwealth of Puerto Rico and the Territory of Guam are not shown).

Nickel and its compounds are naturally present in the Earth's crust, and releases to the atmosphere occur from natural discharges such as windblown dust and volcanic eruptions, as well as from anthropogenic activities. It is estimated that 8.5 million kg of nickel are emitted into the atmosphere from natural sources such as windblown dust, volcanoes, and vegetation each year (Bennett 1984; Schmidt and Andren 1980). Five times that quantity is estimated to come from anthropogenic sources (Nriagu and Pacyna 1988). The burning of residual and fuel oil is responsible for 62% of anthropogenic emissions, followed by nickel metal refining, municipal incineration, steel production, other nickel alloy production, and coal combustion (Bennett 1984; Schmidt and Andren 1980). Table 6-1 lists releases from facilities in the United States that produced, processed, or used nickel metal in 2002, according to TRI (TRI02 2004). These releases, which totaled 6,792,299 pounds (3,081 metric tons), were distributed as follows: 82.2% to land, 6.0% to air, 2.2% to water, and 0.8% to underground injection. Table 6-2 lists releases from facilities in the United States that produced, processed, or used nickel compounds in 2002, according to TRI (TRI02 2004). These releases, which totaled 37,558,704 pounds (17,037 metric tons), were distributed as follows: 87.1% to land, 2.5% to air, 1.4% to water, and 1.7% to underground injection. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

The general population is exposed to low levels of nickel in ambient air, water, and food. Exposure also occurs from smoking. The general population takes in most nickel through food. The average daily dietary nickel intake for U.S. diets is 69–162 μg (NAS 2002; O'Rourke et al. 1999; Pennington and Jones 1987; Thomas et al. 1999). These values agree with those from European studies. Typical average daily intakes of nickel from drinking water and inhalation of air are approximately 8 and 0.04 μg , respectively.

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



Derived from HazDat 2005

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Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Nickel^a

State ^c	RF ^d	Reported amounts released in pounds per year ^b							
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	Total release		
							On-site ^j	Off-site ^k	On- and off-site
AL	58	2,610	1,302	0	81,145	256	3,786	81,526	85,312
AR	38	15,621	665	0	11,572	13,210	16,176	24,893	41,069
AZ	19	1,421	6	0	674,841	5	670,775	5,498	676,273
CA	94	1,886	3,377	24,776	223,027	17,568	216,055	54,578	270,634
CO	15	97	58	0	1,232	19,277	357	20,308	20,665
CT	47	2,514	4,355	0	58,026	18,330	3,124	80,102	83,225
DE	2	5	0	0	750	250	5	1,000	1,005
FL	26	2,188	340	3,833	8,429	29,663	9,480	34,973	44,453
GA	36	2,617	1,072	0	3,459	11,575	3,222	15,502	18,724
IA	62	4,459	1,623	0	38,465	12,020	5,880	50,687	56,568
ID	5	70	5	0	238,979	0	239,049	5	239,054
IL	129	8,057	19,525	255	111,752	16,157	13,473	142,273	155,746
IN	154	37,078	3,914	500	2,026,732	43,905	42,673	2,069,457	2,112,130
KS	24	2,422	94	0	10,671	594	11,730	2,051	13,781
KY	54	2,220	2,555	0	58,811	15,529	2,701	76,414	79,115
LA	33	917	899	0	64,942	2,940	57,072	12,626	69,698
MA	41	1,866	983	0	33,468	27,945	2,459	61,803	64,262
MD	13	72	40	0	728	1,418	91	2,167	2,258
ME	8	242	69	0	4,585	4,122	263	8,755	9,018
MI	115	17,489	6,921	0	110,495	32,153	20,683	146,374	167,057
MN	44	658	312	0	1,441	255	910	1,756	2,666
MO	51	7,304	2,103	0	7,801	1,001	10,464	7,745	18,209
MS	25	5,243	127	0	2,326	0	5,655	2,041	7,697
MT	1	40	0	0	16,000	0	16,040	0	16,040
NC	68	965	2,477	0	52,612	26,814	21,099	61,769	82,868
ND	5	34	5	0	2,554	250	37	2,806	2,843
NE	24	2,390	586	0	15,052	192	2,465	15,755	18,220
NH	16	1,000	8,364	0	330	38,540	1,009	47,225	48,234
NJ	22	4,408	2,287	0	8,664	52,540	4,414	63,485	67,899
NM	4	482	7	0	275	7	734	37	771
NV	10	1,040	5	0	64,280	0	40,214	25,111	65,325
NY	67	10,149	3,763	0	37,047	21,878	16,151	56,685	72,836
OH	212	20,209	13,783	5,478	708,223	11,067	196,744	562,016	758,759
OK	66	16,142	190	0	50,733	0	45,194	21,871	67,065
OR	14	2,511	919	0	58,520	5	2,623	59,332	61,955
PA	209	203,216	6,538	0	68,001	55,213	206,110	126,858	332,967

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Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Nickel^a

State ^c	RF ^d	Reported amounts released in pounds per year ^b							
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	Total release		
							On-site ^j	Off-site ^k	On- and off-site
PR	4	0	0	0	0	0	0	0	0
RI	7	266	505	0	0	500	271	1,000	1,271
SC	52	3,633	1,226	0	192,091	643	12,882	184,710	197,593
SD	6	324	5	0	47	0	324	52	376
TN	52	1,467	11,413	0	54,393	1,932	9,685	59,520	69,205
TX	121	6,327	28,697	20,343	211,220	82,910	42,933	306,562	349,495
UT	13	297	267	0	760	0	797	528	1,325
VA	25	1,082	2,490	0	13,393	2,702	5,899	13,768	19,667
VT	5	10	10	0	0	16,186	10	16,196	16,206
WA	20	794	716	0	23,067	2,809	1,482	25,904	27,386
WI	147	10,440	16,873	0	185,992	15,681	21,180	207,806	228,986
WV	13	77	252	0	18,704	1,535	18,629	1,939	20,568
WY	3	53	1	0	25,759	7	25,812	8	25,820
Total	2,279	404,413	151,725	55,185	5,581,392	599,585	2,028,824	4,763,475	6,792,299

Source: TRI02 2004 (Data are from 2002)

^aThe TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

^bData in TRI are maximum amounts released by each facility.

^cPost office state abbreviations are used.

^dNumber of reporting facilities.

^eThe sum of fugitive and point source releases are included in releases to air by a given facility.

^fSurface water discharges, wastewater treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

^gClass I wells, Class II-V wells, and underground injection.

^hResource Conservation and Recovery Act (RCRA) subtitle C landfills; other on-site landfills, land treatment, surface impoundments, other land disposal, other landfills.

ⁱStorage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

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

^kTotal amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

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Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Nickel Compounds^a

State ^c	Reported amounts released in pounds per year ^b						Total release		
	RF ^d	Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	On-site ^j	Off-site ^k	On- and off-site
AK	3	56	221	0	543,911	0	544,124	64	544,188
AL	31	10,093	5,431	501	864,693	71,756	867,989	84,485	952,474
AR	15	11,912	624	0	810,593	30,419	761,710	91,838	853,548
AZ	12	2,647	5	100,000	5,922,548	505	6,011,495	14,210	6,025,705
CA	73	6,129	8,742	4,981	1,102,665	42,528	1,038,435	126,611	1,165,045
CO	7	499	92	0	52,244	47	33,972	18,910	52,882
CT	18	1,586	2,837	0	114,292	49,426	2,503	165,638	168,141
DC	1	0	0	0	18	0	0	18	18
DE	7	19,291	23,985	0	126,040	23,795	119,068	74,043	193,111
FL	23	144,268	4,246	0	2,534,663	4,052	2,629,871	57,358	2,687,229
GA	24	7,599	15,428	0	606,137	132	610,622	18,673	629,295
HI	2	64,800	10	0	4,022	0	64,810	4,022	68,832
IA	18	6,529	28,253	0	156,841	49,686	145,002	96,307	241,309
ID	4	1,490	56	0	33,000	0	34,495	51	34,546
IL	89	18,190	13,206	0	752,162	127,262	481,610	429,210	910,820
IN	76	31,891	19,303	490	1,937,458	187,004	1,524,230	651,917	2,176,146
KS	13	2,608	280	0	64,708	292	66,981	907	67,889
KY	40	23,463	12,224	0	1,784,073	80,688	1,255,775	644,673	1,900,448
LA	35	58,235	7,085	9,841	364,170	474,747	311,507	602,571	914,078
MA	16	15,582	1,270	0	96,020	8,135	39,054	81,953	121,007
MD	11	28,308	2,733	319	10,225	148,413	40,717	149,281	189,998
ME	2	50	3,336	0	6	80	50	3,422	3,472
MI	70	18,024	42,115	0	580,122	90,302	282,080	448,483	730,563
MN	22	14,786	5,678	0	228,322	67,133	98,965	216,954	315,919
MO	32	8,476	2,669	0	661,528	21,698	597,580	96,791	694,371
MS	11	3,859	1,235	72,000	87,969	907	99,004	66,966	165,970
MT	7	2,468	0	101,419	770,075	3,775	431,813	445,924	877,737
NC	30	9,046	4,179	0	551,706	8,848	562,930	10,850	573,780
ND	4	4,159	10	0	128,699	1,800	75,869	58,799	134,668
NE	8	209	1,554	0	127,490	41,645	127,720	43,178	170,898
NH	5	376	126	0	11,192	45	1,781	9,958	11,739
NJ	15	2,415	5,661	0	62,541	9,865	33,721	46,760	80,481
NM	3	339	1	0	112,800	0	73,140	40,000	113,140
NV	10	8,403	930	0	2,568,163	0	2,577,480	16	2,577,496
NY	33	10,228	49,939	0	233,794	136,288	270,034	160,216	430,250
OH	95	21,520	122,772	271,001	2,122,342	243,006	1,221,840	1,558,801	2,780,641

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Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Nickel Compounds^a

State ^c	Reported amounts released in pounds per year ^b								
	RF ^d	Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	Total release		
							On-site ^j	Off-site ^k	On- and off-site
OK	17	9,129	1,800	0	264,634	14,331	238,243	51,651	289,894
OR	9	1,618	264	0	39,697	0	34,682	6,897	41,578
PA	113	90,020	40,145	0	2,021,526	298,951	553,237	1,897,405	2,450,642
PR	6	85,852	2,704	0	8,914	3,300	88,556	12,214	100,770
RI	7	254	3,147	0	447	5,099	814	8,133	8,947
SC	27	5,666	12,734	0	208,779	86,978	178,444	135,713	314,158
SD	1	208	0	0	19,000	0	19,208	0	19,208
TN	38	14,291	14,597	0	721,360	11,733	544,837	217,144	761,981
TX	98	27,305	10,954	71,192	1,050,243	217,862	777,048	600,507	1,377,555
UT	10	2,374	3,450	0	891,742	80	897,517	129	897,646
VA	20	55,129	8,637	0	314,676	37,945	371,633	44,753	416,387
VI	1	227	0	0	3,047	0	1,703	1,571	3,274
WA	7	650	1,047	7	143,228	234	137,877	7,289	145,166
WI	46	5,615	9,474	0	41,811	108,006	8,384	156,521	164,906
WV	18	80,986	21,617	2,681	745,233	20,087	647,928	222,676	870,604
WY	3	3,260	0	0	128,797	6,100	132,057	6,100	138,157
Total	1,286	942,117	516,804	634,432	32,730,365	2,734,986	27,670,143	9,888,561	37,558,704

Source: TRI02 2004 (Data are from 2002)

^aThe TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

^bData in TRI are maximum amounts released by each facility.

^cPost office state abbreviations are used.

^dNumber of reporting facilities.

^eThe sum of fugitive and point source releases are included in releases to air by a given facility.

^fSurface water discharges, wastewater treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

^gClass I wells, Class II-V wells, and underground injection.

^hResource Conservation and Recovery Act (RCRA) subtitle C landfills; other on-site landfills, land treatment, surface impoundments, other land disposal, other landfills.

ⁱStorage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

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

^kTotal amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

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The highest general population exposures to nickel are typically observed in communities surrounding nickel refineries. This is reflected, for example, in the intakes of nickel from water and air reported in Sudbury, Ontario, Canada, of 140 and 15 $\mu\text{g}/\text{day}$, respectively. However, this source of exposure to nickel is not a concern for U.S. populations, due to the absence of refinery operations in the United States. Other potential sources of nickel exposure are from contaminated intravenous fluids, dialysis, and leaching and corrosion of nickel from prostheses.

Occupational exposure to nickel may occur by dermal contact or by inhalation of aerosols, dusts, fumes, or mists containing nickel. Dermal contact may also occur with nickel solutions, such as those used in electroplating, nickel salts, and nickel metal or alloys. Nickel-containing dust may be ingested where poor work practices exist or where poor personal hygiene is practiced. A National Occupational Exposure Survey (NOES) conducted by NIOSH from 1981 to 1983 estimates that 727,240 workers are potentially exposed to some form of nickel metal, alloys, salts, or inorganic nickel compounds in the United States (NIOSH 1990). The forms of nickel that these workers were probably exposed to and the levels of exposure for different industries and operations were reviewed by Warner (1984) and IARC (1990).

Information on nickel exposure from hazardous waste sites is lacking. The most probable route of exposure from hazardous waste sites would be from consumption of contaminated drinking water, inhalation of dust, dermal contact with bath/shower water, soil, or dust, and ingestion of nickel-contaminated soil. Groundwater contamination may occur where the soil has a coarse texture and where acid waste, such as waste from plating industries, is discarded. However, there is no information linking this source of nickel contamination in groundwater to levels of nickel in drinking water that would be of concern ($>50 \mu\text{g}/\text{L}$).

Nickel releases to the atmosphere are mainly in the form of aerosols that cover a broad spectrum of sizes. Particulates from power plants tend to be smaller than those from smelters (Cahill 1989; Schroeder et al. 1987). Atmospheric aerosols are removed by gravitational settling and dry and wet deposition. Submicron particles may have atmospheric half-lives as long as 30 days (Schroeder et al. 1987). Monitoring data confirm that nickel can be transported far from its source (Pacyna and Ottar 1985). Average ambient air nickel concentrations in the United States measured during 1977–1982 ranged between 7 and 12 ng/m^3 (EPA 1986a). A recent estimate of ambient nickel concentrations in the United States based on data collected in 1996 is 2.22 ng/m^3 (EPA 2003u). Nickel concentrations in air particulate matter in remote, rural, and U.S. urban areas have been found in the ranges of 0.01–60, 0.6–

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78, and 1–328 ng/m³, respectively (Schroeder et al. 1987). Nickel concentrations in indoor air are typically <10 ng/m³ (Graney et al. 2004; Kinney et al. 2002; Koutrakis et al. 1992; Van Winkle and Scheff 2001).

The form of nickel emitted to the atmosphere varies according to the type of source. Nickel species associated with combustion, incineration, and metals smelting and refining are often complex nickel oxides, nickel sulfate, and metallic nickel, and in more specialized industries, the species commonly found are nickel silicate, nickel subsulfide, and nickel chloride (EPA 1985a).

Uncontaminated freshwater and seawater generally contain about 0.300 µg/L of nickel (Barceloux 1999). Concentrations of nickel in drinking water commonly range from 0.55 to 25 µg/L and average between 2 and 4.3 µg/L. The concentration of nickel in rain has been reported as ≤1.5 µg/L. Concentrations of nickel in snow in Montreal, Canada, ranged from 2 to 300 ppb (2,300 µg/L) (Landsberger et al. 1983).

Nickel is a natural constituent of soil; levels vary widely depending on local geology and anthropogenic input. The typical concentrations of nickel reported in soil range from 4 to 80 ppm. Nickel may be transported into streams and waterways from the natural weathering of soil as well as from anthropogenic discharges and runoff. This nickel accumulates in sediment. Nickel levels in surface water are low. In some studies, nickel could not be detected in a large fraction of analyzed samples. Median nickel concentrations in rivers and lakes range from ≈0.5 to 6 µg/L. Levels in groundwater appear to be similar to those in surface water. Levels in seawater are typically 0.1–0.5 µg/L.

The speciation and physicochemical state of nickel is important in considering its behavior in the environment and availability to biota. For example, the nickel incorporated in some mineral lattices may be inert and have no ecological significance. Most analytical methods for nickel do not distinguish the form of nickel; the total amount of nickel is reported, but the nature of the nickel compounds and whether they are adsorbed to other material is not known. This information, which is critical in determining nickel's liability and availability, is site specific. Therefore, it is impossible to predict nickel's environmental behavior on a general basis.

Little is known concerning the chemistry of nickel in the atmosphere. The probable species present in the atmosphere include soil minerals, nickel oxide, and nickel sulfate (Schmidt and Andren 1980). In aerobic waters at environmental pHs, the predominant form of nickel is the hexahydrate Ni(H₂O)₆²⁺ ion (Richter and Theis 1980). Complexes with naturally occurring anions, such as OH⁻, SO₄²⁻, and Cl⁻, are formed to

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a small degree. Complexes with hydroxyl radicals are more stable than those with sulfate, which in turn are more stable than those with chloride. $\text{Ni}(\text{OH})_2^0$ becomes the dominant species above pH 9.5. In anaerobic systems, nickel sulfide forms if sulfur is present, and this limits the solubility of nickel. In soil, the most important sinks for nickel, other than soil minerals, are amorphous oxides of iron and manganese. The mobility of nickel in soil is site specific depending mainly on soil type and pH. The mobility of nickel in soil is increased at low pH. At one well-studied site, the sulfate concentration and the surface area of soil iron oxides were also key factors affecting nickel adsorption (Richter and Theis 1980).

6.2 RELEASES TO THE ENVIRONMENT

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

Most analytical methods for nickel in environmental samples do not distinguish between compounds of nickel or the nature of its binding to soil and particulate matter. It is generally impossible to say with certainty what forms of nickel are released from natural and anthropogenic sources, what forms are deposited or occur in environmental samples, and to what forms of nickel people are exposed. The form of nickel has important consequences as far as its transport, transformations, and bioavailability are concerned.

6.2.1 Air

Estimated releases of 404,413 pounds (~183 metric tons) of nickel and 942,117 pounds (~427 metric tons) of nickel compounds to the atmosphere from 2,279 and 1,286 domestic manufacturing and processing facilities in 2002, respectively, accounted for about 6.0 and 2.5% of the estimated total environmental releases, respectively, from facilities required to report to the TRI (TRI02 2004). These releases are summarized in Tables 6-1 and 6-2.

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Nickel and its compounds are naturally present in the Earth's crust, and releases to the atmosphere occur from natural processes such as windblown dust and volcanic eruption, as well as from anthropogenic activities. These latter releases are mainly in the form of aerosols. It is important to consider the background levels that are due to natural sources and distinguish them from levels that may result from anthropogenic activities. It is estimated that 8.5 million kg of nickel are emitted into the atmosphere from natural sources each year (Bennett 1984; Schmidt and Andren 1980). Based on this value, sources of nickel have been estimated as follows: windblown dust, 56%; volcanoes, 29%; vegetation, 9%; forest fires, 2%; and meteoric dust, 2%. A more recent and higher estimate of 30 million kg/year has been given for emission of nickel into the atmosphere from natural sources (Duce et al. 1991; Giusti et al. 1993). Anthropogenic sources of atmospheric nickel include nickel mining, smelting, refining, production of steel and other nickel-containing alloys, fossil fuel combustion, and waste incineration.

Emissions factors (i.e., kg of nickel emissions per unit consumption or production) have been estimated for various source categories, and these have been used to estimate worldwide emissions (Nriagu and Pacyna 1988). According to Schmidt and Andren (1980), annual anthropogenic emissions are estimated to contain 43 million kg of nickel (median value), 1.4 times the natural emission rate of 30 million kg/year. Nriagu and Pacyna (1988) estimate annual anthropogenic emissions as 55.6 million kg. The nickel emission factor for burning residual and fuel oil is estimated to be 0.03 kg/ton, yielding nickel emissions of 26.7 million kg/year or 62% of the total anthropogenic emissions (Schmidt and Andren 1980). The estimated contributions of other anthropogenic sources of nickel are nickel metal and refining, 17%; municipal incineration, 12%; steel production, 3%; other nickel-containing alloy production, 2%; and coal combustion, 2% (Bennett 1984; Schmidt and Andren 1980). Wood combustion is also an important source of nickel emissions (Nriagu and Pacyna 1988).

Based on data contained in EPA's 1996 National Toxics Inventory (NTI), which is compilation of emissions data obtained from TRI, state and local databases, and other studies required by the Clean Air Act (CAA), it is estimated that emissions of nickel compounds into air totaled 1,170 tons per year in the United States (EPA 2000). Of this total, 1,196 tons of nickel compounds per year were derived from urban sources, with the major contributors coming from stationary sources that release 10 or more tons of nickel compounds per year. On-road mobile sources, such as cars, motorcycles, trucks, and buses, accounted for only 10 tons per year of nickel released to air, whereas nonroad mobile sources, such as airplanes, boats, and lawn mowers, accounted for a release of 66 tons of nickel compounds per year.

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Deposition of metals around large smelter complexes is a significant local problem. For example, at the Copper Cliff smelter in Sudbury, Ontario, it is estimated that 42% of nickel particulates emitted from the 381-m stack are deposited within a 60-km radius of the smelter (Taylor and Crowder 1983). The Copper Cliff smelter, one of three large nickel sources in the Sudbury area, emits 592 pounds (269 kg) of nickel per day.

A typical, modern, coal-fired power plant emits ≈ 25 μg nickel per Megajoule (MJ) of power produced, compared with 420 $\mu\text{g}/\text{MJ}$ for an oil-fired plant (Hasanen et al. 1986). The nickel concentration in stack emissions from a modern coal-fired power plant with an electrostatic precipitator was 1.3 $\mu\text{g}/\text{m}^3$ (Lee et al. 1975). In a case study of the emissions of metals from an average sized coal-burning electric power plant (650 MW at a capacity factor of 67%) equipped with an electrostatic precipitator (ESP), 100 kg/year of nickel is emitted into air (Rubin 1999). These nickel emissions are reduced to 16 kg/year for plants that are fitted with a wet lime/limestone flue gas desulfurization system downstream from the ESP. High-sulfur eastern coal has a higher nickel content than low-sulfur western coal, so power plants using eastern coal emit more nickel than those using western coal (QueHee et al. 1982).

It is estimated that in 1999, 570,000 tons of nickel were released from the combustion of fossil fuels worldwide (Rydh and Svärd 2003). Of this, 326 tons were released from electric utilities (Leikauf 2002).

From a public health point of view, the concentration of nickel associated with small particles that can be inhaled into the lungs is of greatest concern. The nickel content of aerosols from power plant emissions is not strongly correlated with particle size (Hansen and Fisher 1980). In one coal plant, 53 and 32% of nickel in emissions were associated with particles <3 and <1.5 μm in diameter, respectively (Sabbioni et al. 1984). Other studies found that only 17–22% of nickel emissions from coal-fired power plants were associated with particles of >2 μm , and that the mass medium diameter (MMD) of nickel-containing particles from a plant with pollution control devices was 5.4 μm (Gladney et al. 1978; Lee et al. 1975). In one study, 40% of the nickel in coal fly ash was adsorbed on the surface of the particles rather than being embedded in the aluminosilicate matrix (Hansen and Fisher 1980). Surface-adsorbed nickel would be more available than embedded nickel.

Nickel emissions from municipal incinerators depend on the nickel content of the refuse and the design and operation of the incinerator. By comparing the nickel content of particles emitted from two municipal incinerators in Washington, DC, with that of atmospheric particulate matter, Greenberg et al. (1978) concluded that refuse incineration is not a major source of nickel in the Washington area. The

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average nickel concentrations in suspended particles from these incinerators ranged from 170 to 200 ppm. Nickel is not primarily associated with very fine or coarse particles. In tests performed under the Canadian National Incinerator Testing and Evaluation Program, 1.0 g nickel/ton refuse was emitted under normal operating conditions; when the combustion chamber operated at low and high combustion temperatures, nickel emissions increased ≤ 2.2 g nickel/ton (Hay et al. 1986). These emissions can be compared with a factor of 0.33 g nickel/ton refuse obtained in a European study (Pacyna 1984). The European study also obtained an emission factor of 1.0 g nickel/ton for sewage sludge incineration.

An increase in nickel emissions over presettlement levels was assessed by dating and analyzing peat cores from a fen located in northern Indiana, which is downwind from the city of Chicago and the industrial complexes of Gary and East Chicago, areas that contain a large steel mill and a coal-fired power plant. The peak accumulation rate was 7.73 mg nickel/m²/year for 1970–1973, a factor of 21 greater than the accumulation rate in presettlement times (A.D. 1339–1656) (Cole et al. 1990).

Some work has been performed to determine the species of nickel present in air emissions from different source categories (EPA 1985a). This has been determined from analyses of dust by x-ray diffraction, scanning electron microscopy, and energy dispersive x-ray analysis or by an assessment of the reactions and transformations possible for the material present and the process conditions. Nickel resulting from oil combustion is primarily nickel sulfate with lesser amounts of complex metal oxides and nickel oxide. Approximately 90% of nickel in fly ash from coal combustion consists of complex (primarily iron) oxides. Nickel silicate and iron-nickel oxides would be expected from the mining and smelting of lateritic nickel ore, whereas nickel matte refining would produce nickel subsulfide and metallic nickel. The primary nickel species from secondary nickel smelting and steel and nickel alloys production is iron-nickel oxide.

Nickel and nickel compounds have been identified in air samples collected from 20 of the 872 NPL hazardous waste sites where nickel or nickel compounds have been detected in environmental media (HazDat 2005). Nickel or nickel compounds have been detected in air offsite of NPL sites at concentrations ranging from 0.4912 to 4,000 ng/m³.

6.2.2 Water

Estimated releases of 151,725 pounds (~69 metric tons) of nickel and 516,804 pounds of nickel compounds (~234 metric tons) to surface water from 2,279 and 1,286 domestic manufacturing and

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processing facilities in 2002, respectively, accounted for about 2.2 and 1.4% of the estimated total environmental releases, respectively, from facilities required to report to the TRI (TRI02 2004). These releases are summarized in Tables 6-1 and 6-2.

Nickel is a natural constituent of soil and is transported into streams and waterways in runoff either from natural weathering or from disturbed soil. Much of this nickel is associated with particulate matter. Nickel also enters bodies of water through atmospheric deposition.

Emission factors have been estimated for the release of trace metals to water from various source categories and these have been used to estimate inputs of these metals into the aquatic ecosystem. The global anthropogenic input of nickel into the aquatic ecosystem for 1983 is estimated to be between 33 and 194 million kg/year with a median value of 113 million kg/year (Nriagu and Pacyna 1988).

A survey of raw and treated waste water from 20 industrial categories indicated that nickel is commonly found in some waste waters. Those industries with mean effluent levels of $>1,000 \mu\text{g/L}$ in raw waste water were inorganic chemicals manufacturing ($20,000 \mu\text{g/L}$), iron and steel manufacturing ($1,700 \mu\text{g/L}$), battery manufacturing ($6,700 \mu\text{g/L}$), coil coating ($1,400 \mu\text{g/L}$), metal finishing ($26,000 \mu\text{g/L}$), porcelain enameling ($19,000 \mu\text{g/L}$), nonferrous metal manufacturing ($<91,000 \mu\text{g/L}$), and steam electric power plants ($95,000 \mu\text{g/L}$) (EPA 1981). Those industries with mean effluent levels $>1,000 \mu\text{g/L}$ in treated waste water were porcelain enameling ($14,000 \mu\text{g/L}$) and nonferrous metal manufacturing ($14,000 \mu\text{g/L}$) (EPA 1981). The maximum levels in treated discharges from these industries were 67,000 and 310,000 $\mu\text{g/L}$, respectively. In addition, four other industrial categories had maximum concentrations in treated discharges $>1,000 \mu\text{g/L}$. These were inorganic chemicals manufacturing ($1,400 \mu\text{g/L}$), iron and steel manufacturing ($7,800 \mu\text{g/L}$), aluminum forming ($20,000 \mu\text{g/L}$), and paint and ink formulation ($80,000 \mu\text{g/L}$).

Domestic waste water is the major anthropogenic source of nickel in waterways (Nriagu and Pacyna 1988). Concentrations of nickel in influents to 203 municipal waste water treatment plants (9,461 observations) ranged from 2 to 111,400 $\mu\text{g/L}$; the median value was $\approx 300 \mu\text{g/L}$ (Minear et al. 1981). From a study of influent streams of a waste water treatment plant in Stockholm, Sweden, it was determined that the waste streams from households (e.g., drinking water) and businesses (e.g., drinking water, car washes, chemical uses) account for 29% of nickel in influent streams (Sörme and Lagerkvist 2002), which is likely to be comparable to what occurs in the United States. Another 31% of the nickel in influent streams is added at the waste water treatment plant through the addition of water treatment

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chemicals. Storm water accounts for between 1 and 5% of the nickel in influent streams. Concentrations in treated effluents were not reported. However, nickel may be removed by chemical precipitation or coagulation treatment in publicly owned treatment works, which reduces nickel releases (EPA 1981). For example, improvements in sewage treatment facilities have attributed to a reduction in the flux of nickel in waste water effluents into the Hudson River estuary, decreasing from 518 kg/day in 1974 to 43 kg/day in 1997 (Sañudo-Wilhelmy and Gill 1999).

Effluent water generated from mining and smelting operations comes from seepage, runoff from tailing piles, or from utility water used for mine operations. These discharges consist mostly of less-soluble silicates and sulfides and readily settle out. Tailing effluents from sulfidic ores are acidic due to the bacterial generation of sulfuric acid from the sulfidic minerals in the tailings, and very high concentrations of soluble nickel sulfate may be released. Tailing waters from the Onaping and Sudbury areas of Ontario, Canada, have an average nickel content of 42,500 µg/L, a factor of 8,300 greater than that found in river water (Mann et al. 1989). Since there is presently no nickel mining of sulfidic ore in the United States, nickel-containing waste water is not generated by this activity. However, past nickel mining may have contributed to nickel entering our waterways and accumulating in sediment. Old tailing piles may contribute to runoff for decades.

In the EPA-sponsored National Urban Runoff Program, in which 86 samples of runoff from 15 cities throughout the United States were analyzed, nickel was found in 48% of runoff samples, at concentrations of 1–182 µg/L (Cole et al. 1984). The geometric mean nickel concentration in runoff water from the cities studied was between 5.8 and 19.1 µg/L. In a more recent study of nickel concentrations in storm runoff water samples taken from different urban source areas, the arithmetic means of the concentrations for dissolved nickel ranged from <1 to 87 µg/L, and from 17 to 55 µg/L for nickel that also included the metal associated with particulates (Pitt et al. 1995).

One of the potentially dangerous sources of chemical release at waste sites is landfill leachate. In a study that looked at leachate from three municipal landfills in New Brunswick, Canada, the results were conflicting. Average nickel concentrations in the three leachates (control) were 28 (45) µg/L, 33 (not detectable) µg/L, and 41 (23) µg/L (Cyr et al. 1987). Sediment at three sites below the leachate outfalls contained 11.9, 37.4, and 71.2 ppm of nickel (dry weight).

Nickel and/or nickel compounds have been identified in surface water samples collected from 292 of the 872 NPL hazardous waste sites where nickel or nickel compounds have been detected in environmental

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media (HazDat 2005). Nickel or nickel compounds have been detected in surface water offsite of NPL sites at concentrations ranging from 2 to 20,000 ppb. Nickel and/or nickel compounds have also been identified in groundwater samples collected from 593 of the 872 NPL hazardous waste sites (HazDat 2005). Nickel or nickel compounds have been detected in groundwater offsite of NPL sites at concentrations ranging from 4.2 to 11,400 ppb.

6.2.3 Soil

Estimated releases of 5.58 million pounds (~5,530 metric tons) of nickel and 32.7 million pounds (~14,800 metric tons) of nickel compounds to soils from 2,279 and 1,286 domestic manufacturing and processing facilities in 2002, respectively, accounted for about 82 and 87% of the estimated total environmental releases, respectively, from facilities required to report to the TRI (TRI02 2004). An additional 55,185 pounds (~25 metric tons) of nickel and 634,432 pounds (~288 metric tons) of nickel compounds, constituting about 0.8% and 1.7% of the total environmental emissions, respectively, were released via underground injection (TRI02 2004). These releases are summarized in Tables 6-1 and 6-2.

Most of the nickel released to the environment is released to land. Emission factors for nickel released to soil have been estimated for various industries (Nriagu and Pacyna 1988). These factors can be used to estimate industrial nickel releases to land. Excluding mining and smelting releases to land, 66% of estimated anthropogenic environmental releases or 325 million kg/year (median) are to soil (Nriagu and Pacyna 1988). Some important sources of nickel released to soil are coal fly ash and bottom ash, waste from metal manufacturing, commercial waste, atmospheric fallout, urban refuse, and sewage sludge.

Based on 1999 production data, the equivalent of 0.6–3.3% of the nickel that was mined that year was used in the manufacture of portable batteries (Rydh and Svärd 2003). This amounts to approximately 17–31 ktons of nickel. Although current battery recycling programs in Europe claim success rates of upwards of 55%, the global recycling rates are typically lower, ranging between 5 and 50%. Therefore, on a global level, more than half of the nickel used in battery production will be disposed of in landfills and other waste sites.

Nickel and/or nickel compounds have been identified in soil samples collected from 443 of the 872 NPL hazardous waste sites where nickel or nickel compounds have been detected in environmental media (HazDat 2005). Nickel or nickel compounds have been detected in soils offsite of NPL sites at concentrations ranging from 2 to 10,522 ppb. Nickel and/or nickel compounds have also been identified

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in sediment samples collected from 302 of the 872 NPL hazardous waste sites (HazDat 2005). Nickel or nickel compounds have been detected in sediments offsite of NPL sites at concentrations ranging from 0.009 to 33,100 ppm.

6.3 ENVIRONMENTAL FATE

It is not always possible to separate the environmental fate processes relating to transport and partitioning from those relating to transformation for a metal and its various compounds and complexes. Because of analytical limitations, investigators rarely identify the form of a metal present in the environment. A change in the transport or partitioning of a metal may result from a transformation. For example, complexation may result in enhanced mobility, while the formation of a less-soluble sulfide would decrease its mobility in water. Adsorption may be the result of strong bonds being formed (transformation) as well as weak ones. Separating data relating to strong and weak adsorption in different sections is awkward and may not always be possible. Section 6.3.1 covers deposition and general adsorption of nickel, and Section 6.3.2 examines areas of environmental fate in which speciation occurs.

6.3.1 Transport and Partitioning

Nickel is released to the atmosphere in the form of particulate matter or adsorbed to particulate matter. It is dispersed by wind and removed by gravitational settling (sedimentation), 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 depends on source characteristics (e.g., stack height), particle size and density, and meteorological conditions.

Gravitational settling governs the removal of large particles ($>5 \mu\text{m}$), whereas smaller particles are removed by other forms of dry and wet deposition. The partitioning between dry and wet deposition depends on the intensity and duration of precipitation, the element in question and its form in the particulate matter, and particle size. The importance of wet deposition relative to dry deposition generally increases with decreasing particle size. Removal of coarse particles may occur in a matter of hours. Small particles within the size range of $0.3\text{--}0.5 \mu\text{m}$ may have an atmospheric half-life as long as 30 days and, therefore, have the potential to be transported over long distances (Schroeder et al. 1987). Evidence for the long-range transport of nickel is provided by the fact that emission sources in North America,

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Greenland, and Europe are responsible for elevated atmospheric nickel concentrations in the Norwegian Arctic during both the summer and winter (Pacyna and Ottar 1985).

Available studies indicate that nickel is broadly distributed among aerosol size groups. It has been concluded, based on the chemical and physical properties of atmospheric particles, that the concentrations of nickel in large particles ($>1 \mu\text{m}$ diameter) that are commonly associated with particulates derived from natural sources are less than concentrations in smaller particles ($<1 \mu\text{m}$ diameter) that are typically derived from anthropogenic sources (Giusti et al. 1993; Scudlark et al. 1994; Stoessel and Michaelis 1986). However, experiments in Ontario showed that nickel is associated with relatively large particles, $5.6 \pm 2.4 \mu\text{m}$ (Chan et al. 1986). A 1970 National Air Surveillance Network study of the average nickel size distribution in six American cities indicated that the mass median diameter (MMD) is $\approx 1.0 \mu\text{m}$ in all six cities (Lee et al. 1972). Although the sampling procedure used in this study may have underestimated large particles (Davidson 1980), it represents one of the few studies involving the size distribution of nickel aerosols in U.S. cities.

Nickel concentration and speciation were investigated in particulate matter collected from an urban environment. The sampling sites in Davie, Florida, are within a high population area (3,837 persons per square mile) that is influenced by a number of stationary and mobile point source emitters of particulate matter, including residual oil- and natural gas-burning power plants, municipal waste incinerators, automobiles, aircraft, and marine vessel traffic (Galbreath et al. 2003). Nickel concentrations of 86 and 140 ppm were measured in total suspended particulates (TSP) and in particulates with a MMD of $10 \mu\text{m}$ (PM_{10}), respectively. The concentration of 140 ppm in the PM_{10} fraction converts to an airborne nickel concentration of 1.5 ng/m^3 . Three nickel species were characterized and measured in the particulate fractions, $\text{NiSO}_4 \cdot x\text{H}_2\text{O}$, NiFe_2O_4 , and NiS . The proportions of these species in the TSP fraction were 40, 50, and 10%, respectively; the proportions in the PM_{10} fraction were 78, 22, and $<5\%$, respectively.

Metal deposition is characterized by large temporal and spatial variability. Deposition can be associated with precipitation (wet deposition) or result from processes such as gravitational settling of dust (dry deposition). Estimated nickel deposition rates range from 0.01 to 0.5 kg/hectare/year ($1\text{--}50 \text{ mg/m}^2/\text{year}$) and from 0.1 to 5.95 kg/hectare/year ($10\text{--}595 \text{ mg/m}^2/\text{year}$) in rural and urban areas, respectively (Schroeder et al. 1987). In the Florida Atmospheric Mercury Study (FAMS) conducted during 1993–1994, bulk deposition rates for nickel varied between 1.700 and $4.130 \text{ mg/m}^2/\text{year}$, depending on local/regional anthropogenic activity (Landing et al. 1995). Nickel deposition from 1980 to 1981 in an industrial area of England where a number of ferrous and nonferrous metal smelting and manufacturing

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works were concentrated had a mean value of 8,800 ng/cm²/year (88 mg/m²/year), a factor of 8–25 above nonurban deposition rates (Pattenden et al. 1982). Wet deposition accounted for half of the deposition. Eighty-one percent of the nickel in rain was dissolved. Schroeder et al. (1987) reported the same percent of dry to wet deposition for nickel, whereas Chan et al. (1986) found that 2.2 times as much wet deposition as dry deposition occurred in Ontario in 1982 with little variability in the ratio across the province. The mean dry deposition rates for southern, central, and northern Ontario in 1982 were 0.25, 0.28, and 0.18 mg/m²/year, respectively. In southern Ontario, Canada, where the average concentration of nickel in rain was 0.557 ppb during 1982, 0.5 mg of nickel 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 nickel in rain were 0.613 and 0.606 ppb, respectively, and the annual wet depositions averaged 0.5 and 0.4 mg/m². Wet and dry deposition of particulates emitted from the Claremont Incinerator in Claremont, New Hampshire, were measured within an area between 2 and 15 km from the incinerator. Wet deposition rates varied between 0.50 and 8.87 µg/m²/day (0.0005–0.00887 mg/m²/day) with a mean value of 3.0 µg/m²/day (0.003 mg/m²/day) and depended on distance from the incinerator and wind weight. The mean wet deposition rate of 3.0 µg/m²/day (0.003 mg/m²/day) was a factor of approximately 19 greater than the mean dry deposition rate of 0.16 µg/m²/day (0.00016 mg/m²/day), which had been calculated from values ranging from 0.067 to 0.29 µg/m²/day (0.000067–0.00029 mg/m²/day) (Feng et al. 2000).

Atmospheric deposition of nickel in coastal waters has been reported. Bulk and wet deposition of nickel into Massachusetts Bay was determined to be 7,200 and 3,000 µg/m²/year (Golomb et al. 1997), respectively, whereas a lower wet deposition rate of 257 µg/m²/year was measured for nickel in Chesapeake Bay (Scudlark et al. 1994). Atmospheric input of nickel into the Great Lakes has been estimated to average 160–590 ng/m²/year (Nriagu et al. 1996).

Wet and dry deposition of nickel into the world's oceans is estimated to be 8–11 and 14–17 gigagrams (10⁹ grams) per year, respectively (Duce et al. 1991). However, atmospheric deposition is only a minor contributor to the flow of nickel into the oceans and coastal waterways as compared to riverine and fluvial input of nickel. The nickel that is carried into oceans in both dissolved and particulate forms through riverine input is rated at 1,411 gigagrams per year, which is a factor of approximately 50 greater than the sum of the wet and dry deposition of nickel of 22–28 gigagrams per year (Duce et al. 1991). In an example of nickel input into Chesapeake Bay, the fluvial input of nickel of 98,700 kg/year (0.0987 gigagrams/year) is 25 times greater than bulk deposition of nickel from the atmosphere (Scudlark et al. 1994). However, for the Great Lakes the atmospheric input of nickel accounts for 60–80% of the

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total anthropogenic input of nickel into Lake Superior, and 20–70% of the total inputs into Lakes Erie and Ontario (Nriagu et al. 1996).

The fate of heavy metals in aquatic systems depends on partitioning between soluble and particulate solid phases. Adsorption, precipitation, coprecipitation, and complexation are processes that affect partitioning. These same processes, which are influenced by pH, redox potential, the ionic strength of the water, the concentration of complexing ions, and the species and concentration of the metal, affect the adsorption of heavy metals to soil (Richter and Theis 1980).

Adsorption of nickel onto suspended particles in water is one of the main removal mechanisms of nickel from the water column. The adsorption of nickel on water-borne particulate matter is in competition with adsorption onto dissolved organic matter, which limits the amount of nickel that can be removed from the water column through the settling of suspended particles (Martino et al. 2003). Much of the nickel released into waterways as runoff is associated with particulate matter; it is transported and settles out in areas of active sedimentation such as the mouth of a river. Additionally, when a river feeds into an estuary, the salinity changes may affect absorptivity due to complexation and competition for binding sites (Bowman et al. 1981). During a 4-month study of Lake Onondaga in Syracuse, New York, 36% of the nickel in the lake was lost to sediment (Young et al. 1982). Seventy-five percent of the nickel load into the lake was soluble and remained in the lake. The soluble nickel is not likely to be as the Ni(II) ion, but is expected to exist as a complex. For example, in an analysis of the speciation of nickel in waste water effluents and runoff discharging into San Francisco Bay, it was found that approximately 20% of soluble nickel was complexed to moderately strong complexing agents, such as humic acid and biopolymers from activated sludges (Sedlak et al. 1997). However, a larger proportion of the nickel, 75% in waste water effluent and 25% in runoff, is found strongly complexed with stability constants that are similar to those found for synthetic chelating agents such as EDTA, DTPA, and phosphonates. Nickel is strongly adsorbed at mineral surfaces such as oxides and hydrous oxides of iron, manganese, and aluminum (Evans 1989; Rai and Zachara 1984). Such adsorption plays an important role in controlling the concentration of nickel in natural waters.

Nickel is strongly adsorbed by soil, although to a lesser degree than lead, copper, and zinc (Rai and Zachara 1984). There are many adsorbing species in soil, and many factors affect the extent to which nickel is adsorbed, so the adsorption of nickel by soil is site specific. Soil properties such as texture, bulk density, pH, organic matter, the type and amount of clay minerals, and certain hydroxides, as well as the extent of groundwater flow, influence the retention and release of metals by soil (Richter and Theis 1980).

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Amorphous oxides of iron and manganese, and to a lesser extent clay minerals, are the most important adsorbents in soil. In alkaline soils, adsorption may be irreversible (Rai and Zachara 1984), which limits nickel's availability and mobility in these soils. For example, in recent studies of nickel speciation in ferromanganese nodules from loess soils of the Mississippi Basin, nickel is found to have a higher partition in the soil nodules than in soil clay matrices (Manceau et al. 2003). This is due to the selective sequestration of nickel by finely divided iron and manganese oxides in goethite and lithiophorite minerals present in the soils. Cations such as Ca^{2+} and Mg^{2+} have been reported to reduce adsorption due to competition for binding sites, whereas anions like sulfate reduce adsorption as a result of complexation. Nickel adsorption depends strongly on metal concentration and pH (Giusti et al. 1993). For each mole of nickel adsorbed by iron and manganese oxide, $\approx 1\text{--}1.5$ moles of hydrogen ions are released (Rai and Zachara 1984). For aluminum oxide, as many as 2.3 moles H^+ are released. Mustafa and Haq (1988) found that the adsorption of nickel onto iron oxide at pH 7.0 was rapid and increased with increasing temperature. They also found that two hydrogen ions are released into a solution when nickel is adsorbed. These studies indicate that while Ni^{2+} is the predominant species in solution, NiOH^+ is preferentially adsorbed, and that both mono- and bidentate complexes may be formed with the iron/manganese/aluminum oxides.

Batch equilibrium studies were performed using seven soils and sediments spiked with varying concentrations of nickel to assess the potential mobility of nickel in contaminated subsoil (LaBauve et al. 1988). The range of Freundlich parameters $K(1/n)$, an adsorption constant, ranged from 739 (0.92) to 6,112 (0.87). One-, two-, and three-parameter models were used to evaluate the relation of soil properties and nickel retention. In the one-parameter model, pH was the best predictor. Cation exchange capacity (CEC) and iron oxide were the best predictors in the two-parameter models, and CEC, iron oxide, and percent clay were the best predictors in the three-parameter models. Nickel was more mobile in the soils than lead, cadmium, and zinc. The retention of nickel to two of the test subsoils diminished in the presence of synthetic landfill leachate, possibly because of complex formation. In another study in which batch adsorption experiments were conducted with a mixture of cadmium, cobalt, nickel, and zinc, and 38 different agricultural soils, taken from three depths at 13 sites, the adsorption constants ranged from 10 to 1,000 L/kg (Anderson and Christensen 1988). Soil pH, and to a lesser extent clay content and the amount of hydrous iron and manganese oxides, most influenced nickel sorption.

In 12 New Mexican soils from agricultural areas and potential chemical waste disposal sites, Freundlich parameters $K(1/n)$ ranged from 8.23 to 650 (0.87–1.18); the median K was 388 (Bowman et al. 1981). The soil with the K of 8.23 was essentially unweathered rock that was not expected to have good

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adsorbing properties. The study concluded that most soils have an extremely high affinity for nickel and that once sorbed, nickel is difficult to desorb, which may indicate covalent bond formation. Sadiq and Enfield (1984b) observed nickel ferrite formation following adsorption. Bowman et al. (1981) found that when nickel levels were >10 ppm, adsorption decreased. High concentrations of chloride decreased adsorption, but not as much as calcium ions, which indicates that calcium competition for sorbing sites is more important than chloride complexation for reducing adsorption. The presence of complexing agents, such as EDTA, dramatically lowers nickel adsorption, which has important implications at waste disposal sites if liquid nickel waste containing chelating agents is released to soil. Chelating agents that are added to soil containing adsorbed nickel appear to have a lesser effect.

The capacity of soil to remove nickel and the nature of the bound nickel were evaluated for 10 mineral and 3 organic soils from the southeastern United States (King 1988). Some soil samples were taken from the subsoil as well as the surface. The amount of adsorbed nickel ranged from 13 to 95%; the low value was found in subsoil, and the high value was found in soil high in organic matter. When extracted with potassium chloride, 5–87% of the nickel was nonexchangeable. Soil pH was the most important factor affecting sorbed and nonexchangeable nickel in all soil horizons. Both King (1988) and Tyler and McBride (1982) found much stronger nickel adsorptivity in organic soil than in mineral soils. Adsorption was improved by the quality and quantity of humus in the soil (Hargitai 1989). Nickel was enriched in humic and fulvic acids from Lake Ontario sediment (Nriagu and Coker 1980). It was estimated that 5–10% of the nickel in this sediment was bound to organic matter.

The leachability of nickel from some soils does not necessarily correlate with the total concentration of nickel in the soil. In an extraction study of soils sampled from the mining and smelting regions of Sudbury, Ontario, the percentage of nickel that is most easily extractable (in acetic acid) varied between 12 and 31% of the total nickel content (220–455 mg/kg) among the different sampling sites (Adamo et al. 1996). The remaining nickel was found in less extractable forms: 6–11% was found to be associated with manganese oxides and easily reducible iron oxides, 6–20% either bound to readily oxidizable organics or sulfides, and the remainder (55–73%) was associated with sulfides as separate grains or inclusions, iron oxide phases, carbon particles, and silicate spheroids. Similarly, in soils that are naturally enriched in heavy metals sampled from the Port MacQuaire region in Australia, the amount of nickel that can be easily extracted from soil samples is only a small fraction of the total nickel content (Lottermoser 2002). Extraction of these soils with EDTA or acetic acid yielded leachable nickel which amounted to between <0.1–4.1 and <0.01%, respectively, of the total nickel concentrations in the soil samples. Use of stronger extraction methods, for example hydrochloric acid, yielded only leachable nickel in percentages

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(0.1–2.4%) equivalent to those found for EDTA. The low amount of acetic acid extractable nickel indicates negligible leaching of this metal from these soils into groundwater and surface waters (Lottermoser 2002).

Amendment of soils with exogenous humic acid reduces mobility of dissolved nickel in soil and also increases the bioavailability of this nickel to plants. Halim et al. (2003) showed that humic acid in soils from nickel-humic acid complexes results in the removal of dissolved and exchangeable nickel from soil water. The extractability of nickel increased with the aging time of the organic material. The increased bioavailability of nickel bound to humic acid is temporary and is thought to occur mainly as the result of preventing nickel from undergoing a transformation into insoluble species in soil.

Nickel (II) is poorly removed from waste water in the activated sludge process because of its high solubility (Stephenson et al. 1987). Only 30–40% of nickel was removed in a pilot activated sludge plant. Nickel removal in activated sludge plants is best correlated with effluent suspended solids (Kempton et al. 1987). Nickel is predominantly soluble in the effluent and is found complexed to humic acid, biopolymers, and other chelating agents (Sedlak et al. 1997).

In order to evaluate the potential of elements to leach from land-spread sewage sludge, Gerritse et al. (1982) studied the adsorption of elements to sandy and sandy loam top soils from water, salt solutions, and sludge solutions. They used metal levels that occurred in the solution phase of sewage sludge, 100–1,000 ppb in the case of nickel. The results indicated that nickel is fairly mobile in these soils; the adsorption constants were ≈ 10 –100 in the sandy soil and a factor of ≈ 10 higher in the sandy loam soil. The presence of sludge increases the mobility of nickel, particularly in sandy and sandy loam soils, which may be because of complexation with dissolved organic compounds (Kaschl et al. 2002) or increased ionic strength (Gerritse et al. 1982). However, land application of nickel-contaminated sludge did not give rise to increased levels of nickel in groundwater (Demirjian et al. 1984). Higher doses and repeated application of nickel-containing sewage sludge did not result in a proportional increase in nickel mobility (Hargitai 1989).

As part of EPA's National Runoff Program in Fresno, California, the soil water and groundwater at depths ≤ 26 m beneath five urban runoff retention/recharge basins were monitored during a 2-year study (Nightingale 1987). The results indicated that there were no significant downward movements of nickel with the recharge water.

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Saline sediments from estuaries often contain pyrite and other readily oxidizable sulfur compounds. When these sediments are oxidized, such as when dredged sediment is exposed to oxygen, sulfuric acid may be produced, which may overwhelm the buffering capacity of the sediment, lower the pH (to pH 3.1 in a laboratory experiment), and dissolve the ferric oxides and hydroxides that entrap heavy metals (DeLaune and Smith 1985). As a result, significant amounts of nickel may be released from the dredged sediments. An analogous pH decrease following exposure to oxygen was not observed in freshwater sediment.

The presence of iron-(di)sulfides in wetland sediments has been associated with increased mobilization of nickel into groundwater during periods of drought in Holland (Lucassen et al. 2002). Dessication of sediments leads to oxidation of iron-(di)sulfides and subsequent acidification of the sediments. When the S/(Ca + Mg) ratios in these sediments rise above 2/3, mobilization of heavy metals like nickel occurs, leading to groundwater concentrations of nickel that exceeded the Dutch signal level of 50 ppb for nickel in 50% of the monitoring locations.

It has been reported that nickel is not accumulated in significant amounts by aquatic organisms (Birge and Black 1980; Zarogian and Johnson 1984). The concentration of nickel in a major carnivorous fish in New York State, the lake trout, was the lowest, and the concentration did not increase appreciably with the age of the fish (Birge and Black 1980). The mean bioconcentration factor (BCF) for three carnivorous fish was 36. The concentration of nickel in mussels and oysters treated with 5 µg nickel/kg of seawater for 12 weeks averaged 9.62 and 12.96 µg nickel/g, respectively, on a dry weight basis (Zarogian and Johnson 1984). When these data are adjusted for controls and the nickel concentration in tissue is expressed on a wet weight basis, the BCF for the mussels and oysters is ≈100. After 2 weeks in flowing seawater, 58 and 38% of the tissue nickel was lost from the mussel and oyster, respectively. No significant loss of nickel occurred during the remainder of the 28-week depuration period. The content of acid volatile sulfide (AVS) in sediment helps determine the bioavailability of metals (Ankley et al. 1991). In studies of nickel and cadmium, the metals were toxic to an amphipod (*Hyallela azteca*) and an oligochaete (*Lumbriculus variegatus*) when the extracted metals/AVS ratio was >1.

In the work of McGeer et al. (2003), BCFs for nickel in various aquatic organisms (e.g., algae, arthropods, mollusks, and fish) was assessed based on whole-body metal concentrations and exposure concentrations that were obtained from the literature. For exposure concentrations within the range of 5–50 µg/L nickel in water, mean BCF values of 106±53 (1 standard deviation [SD]) were obtained. When the authors also included data for exposure concentrations outside the range of 5–50 µg/L, a BCF value of

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157±135 was obtained. The authors noted that the BCF values were inversely correlated with the exposure concentrations, where the highest BCF values were obtained at the lowest exposure concentrations. There was no evidence that nickel biomagnifies in aquatic food webs and, in fact, there is evidence to indicate that the nickel concentrations in organisms decrease with increasing trophic level (McGeer et al. 2003; Suedel et al. 1994).

As part of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program, there was no statistically significant correlation between nickel concentrations in bed-sediments collected from streams and rivers in both the Northern Rockies Intermontane Basin study area and the New Jersey study area, and nickel concentrations measured in liver and fillet samples taken from fish collected in the same study areas (USGS 2000a, 2000b). Also, nickel concentrations in fish liver and fillet samples were at or below the detection limits (<0.1–0.3 µg/g, dry weight) for nickel in these studies and are much lower than the concentrations of nickel measured in bed-sediments, which ranged from 12 to 43 µg/g (wet weight).

Uptake and accumulation of nickel into various plant species is known to occur. For example, Peralta-Videa et al. (2002) report the accumulation of nickel in alfalfa grown from soils contaminated with a mixture of four metals (e.g., Cd(II), Cu(II), Ni(II), and Zn(II)) at a loading of 50 mg/kg for each metal. Concentration ratios of nickel in plant versus soil (based on dry weights) ranged between 22 and 26 over a pH range of 4.5–7.1. As with most plant species that hyperaccumulate metals, the alfalfa actively removes and translocates heavy metals, like nickel, from the roots to the shoots. The uptake of nickel into plants is modulated by the acidity (pH) of the soil. Smith (1994) showed that nickel concentrations in rye grass were reduced by a factor of three as the soil pH was raised from 4 to 7. This is thought to be due to a decrease in bioavailability of nickel with increasing pH. The bioavailability of nickel to plants is also affected by soil type. Weng et al. (2004) found that the bioavailability of nickel to oat plants grown in soil rich in organic matter is half that of sandy or clay soils in the pH range of 4.4–7.0. These differences in bioavailability are attributed to a stronger binding of nickel to organic matter than to the silicates and iron hydroxides/oxides in clay and sand under the acidic conditions of the experiment.

Two studies concerning levels in voles and rabbits living on sludge-amended land did not indicate any accumulation of nickel in these herbivores or in the plants they fed upon (Alberici et al. 1989; Dressler et al. 1986). The lack of significant bioaccumulation of nickel in aquatic organisms, voles, and rabbits indicates that nickel is not biomagnified in the food chain.

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6.3.2 Transformation and Degradation

Analytical methods do not generally allow identification of the precise form of nickel present in environmental samples or an assessment of the transformations that may occur. Sequential extraction techniques are sometimes employed to determine how tightly nickel is bound to particles or in environmental matrices. Using different and progressively stronger extracting agents, the fractions of a sample that are exchangeable, adsorbed, easily reducible, moderately reducible, or organically bound carbonates, sulfides, and residual can be determined (Rudd et al. 1988; Rybicka 1989).

6.3.2.1 Air

Little is known about the chemical forms and physical and chemical transformations of trace elements in the atmosphere primarily because analytical methods provide information concerning the metal content rather than the specific compounds or species. In the absence of specific information, it is generally assumed that elements of anthropogenic origin, especially those emanating from combustion sources are present as the oxide, and nickel oxide has been identified in industrial emissions (Schroeder et al. 1987). Windblown dust particles may contain nickel in mineral species, which often contain nickel as the sulfide. Increases in the concentration of nickel in Sequoia National Park in California during rain coming from the south correlated with a sharp (7–13 times greater concentration) increase in sulfate (Cahill 1989). Nickel sulfate is a probable atmospheric species resulting from the oxidation of nickel in the presence of sulfur dioxide (Schmidt and Andren 1980).

The form of nickel in particles from different industries varies. The mineralogical composition, chemical content, and form of dusts from nine industries in Krakow, Poland, were examined (Rybicka 1989). The chemical form of a particle-associated heavy metal that was assessed by a five-step extraction scheme classified the metal as exchangeable, easily reducible (manganese oxides, partly amorphous iron oxyhydrates and carbonates), moderately reducible (amorphous and poorly crystallized iron oxyhydrates), organically bound or sulfidic, and residual. Dusts from power plants had a silicate characteristic with quartz and mullite predominant. Approximately 90% of the nickel from these facilities was in the residual fraction. Only 40–60% of the nickel from metallurgical, chemical, and cement plants was in the residual fraction. Essentially none of the nickel from any of the industries was in an organic/sulfidic fraction. Dusts from metallurgical, chemical, and cement plants contained between 0 and 10% (typically 5%) of the nickel in the relatively mobile, cation-exchangeable fraction. Thirty percent of the nickel in dust from a slag processing facility was in this form.

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6.3.2.2 Water

In natural waters, nickel primarily exists as the hexahydrate. While nickel forms strong, soluble complexes with OH^- , SO_4^{2-} , and HCO_3^- , these species are minor compared with hydrated Ni^{2+} in surface water and groundwater with $\text{pH} < 9$ (Rai and Zachara 1984). Under anaerobic conditions, such as may exist in deep groundwater, nickel sulfide would reduce free aqueous nickel concentrations to low levels.

Precipitation can remove soluble nickel from water. In aerobic waters, nickel ferrite is the most stable compound (Rai and Zachara 1984). Nickel may also be removed by coprecipitation with hydrous iron and manganese oxides. Nickel removed by precipitation and coprecipitation settles into the sediment.

Nickel in sediment may be strongly bound or present in a removable form. A metal's form in soil or sediment and its availability are determined by measuring the extractability of the metal with different solvents. Sediment samples from western Lake Ontario were analyzed in regard to the compositional associations of nickel by a series of sequential extractions (Poulton et al. 1988). The mean nickel percentages in the various fractions were as follows: exchangeable, 0.7 ± 1.4 ; carbonate, 0.0; iron or manganese oxide-bound, 0.0; organic-bound, 7.4 ± 4.1 ; and residual, 91.9 ± 4.5 . The nickel concentration in 450 uncontaminated estuarine and coastal marine sites in the southeastern United States covaried significantly with the aluminum concentration, suggesting that natural aluminosilicates are the dominant natural metal-bearing phase in some aquatic systems (Windom et al. 1989). In 13 random samples of bottom sediment from the highly industrialized Meuse River in The Netherlands, between 0 and 88% (median 33%) of the nickel was removable at low pH, showing the great variability of nickel to adsorb to sediments (Mouvet and Bourg 1983).

Nickel removed by coprecipitation can be remobilized by microbial action under anaerobic conditions (Francis and Dodge 1990). Remobilization results from enzymatic reductive dissolution of iron with subsequent release of coprecipitated metals. A lowering of pH as a result of enzymatic reactions may indirectly enhance the dissolution of nickel. Experiments using mixed precipitates with goethite ($\alpha\text{-FeOOH}$) indicated that a *Clostridium* species released 55% of the coprecipitated nickel after 40 hours. Similarly, precipitated nickel sulfides in sediment can be mobilized through sulfur oxidation by *Thiobacilli* (Wood 1987). In this case, the oxidized sulfur may produce H_2SO_4 and decrease the pH.

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6.3.2.3 Sediment and Soil

An analysis of the thermodynamic stability models of various nickel minerals and solution species indicates that nickel ferrite is the solid species that will most likely precipitate in soils (Sadiq and Enfield 1984a). Experiments on 21 mineral soils supported its formation in soil suspensions following nickel adsorption (Sadiq and Enfield 1984b). The formation of nickel aluminate, phosphate, or silicate was not significant. Ni^{2+} and $\text{Ni}(\text{OH})^+$ are major components of the soil solution in alkaline soils. In acid soils, the predominant solution species will probably be Ni^{2+} , NiSO_4 , and NiHPO_4 (Sadiq and Enfield 1984a).

A large percentage of nickel in sewage sludges exists in a form that is easily released from the solid matrix (Rudd et al. 1988). Although the availability of nickel to plants grown in sludge-amended soil is correlated with soil-solution nickel, it is only significantly correlated with DTPA-extractable nickel (Adams and Kissel 1989).

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

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

6.4.1 Air

Mean ambient air concentrations of nickel typically range between 6 and 20 ng/m^3 and can be high as 150 ng/m^3 near anthropogenic sources of airborne nickel (Barceloux 1999). Schroeder et al. (1987) reported nickel concentrations in particulate matter in the U.S. atmosphere of 0.01–60, 0.6–78, and 1–328 ng/m^3 in remote, rural, and urban areas, respectively. Nickel concentrations in particulate matter ($\text{PM}_{2.5-8}$), collected in Spokane, Washington, from January 1995 to March 1999, averaged 1.2 ± 0.9 (1 SD) ng/m^3 (Claiborn et al. 2002). Based on emission data contained in the EPA 1996 NTI database, an average concentration of nickel in ambient air in the contiguous United States was estimated

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to be 2.22 ng/m^3 (median concentration= 0.948 ng/m^3) (EPA 2003u). The five states with the highest average concentrations of nickel in ambient air were (ng/m^3): West Virginia (6.60), Utah (4.42), Delaware (4.10), New York (3.80), and Pennsylvania (3.69); the five states with the lowest concentrations were: Wyoming (0.127), South Dakota (0.157), North Dakota (0.211), Montana (0.311), and Vermont (0.311). Annual mean nickel concentrations in 11 Canadian cities measured during 1987–1990 ranged from 1 to 20 ng/m^3 , while at a rural location the mean nickel concentration was 1 ng/m^3 (CEPA 1994). In another Canadian study, mean exposure concentrations for nickel in air for residents living near copper smelters and refineries and zinc plants ranged between 0.005 and $0.151 \mu\text{g/m}^3$ (5 – 151 ng/m^3) in comparison to background levels of $0.00069 \mu\text{g/m}^3$ (0.69 ng/m^3) (Newhook et al. 2003). Annual average nickel concentrations at three remote sites in the arctic region of Canada ranged from 0.14 to 0.45 ng/m^3 (Barrie and Hoff 1985). Levels of nickel and other anthropogenic species peaked during January and February, possibly indicating the significance of combustion sources. Nickel levels in the air at three native villages in northern Alberta, Canada, were 0.779 ± 0.774 , 1.1 ± 0.57 , and $4.97 \pm 9.2 \text{ ng/m}^3$, indicating that air concentrations of nickel can be highly variable (Moon et al. 1988).

According to the EPA's National Air Surveillance Network (NASN) report for 1977, 1978, and 1979, median nickel concentrations were below the detection limit for urban and nonurban samples except for 1978; during 1978, the urban median was 6 ng/m^3 (Evans et al. 1984). The detection limit for inductively-coupled-plasma atomic emission spectroscopy (ICP-AES), the method used in the EPA study, was 1 ng/m^3 (EPA 1986a; Evans et al. 1984). In the EPA study, 10,769 urban samples and 1,402 nonurban 24-hour air samples were analyzed. Five percent of the urban samples were >33 , 32 , and 30 ng nickel/m^3 for 1977, 1978, and 1979, respectively; 5% of the nonurban samples were >10 , 10 , and 6 ng/m^3 , respectively, for these 3 years. Ninety-nine percent of the urban and nonurban samples for these 3 years did not exceed 68 and 52 ng/m^3 , respectively (Evans et al. 1984). Combined urban and nonurban measurements for the 99th percentile from the NASN (1977–1979) and its successor, the National Air Monitoring Filter Sites (NAMFS) (1980–1982), showed a sharp decline from 62 and 67 ng/m^3 in 1977 and 1978 to 23 and 30 ng/m^3 in 1981 and 1982. Mean levels for the combined urban and nonurban sites over the 6-year period ranged from 7 to 12 ng/m^3 (EPA 1986a). According to the NASN data for 1965–1968, the average atmospheric nickel concentration in the air of 28 cities ranged from 3 to 90 ng/m^3 , with an overall average of 26 ng/m^3 (NAS 1975). These data suggest that atmospheric nickel concentrations in the United States have been declining. No reason for this downward trend was suggested (EPA 1986a).

The most intensive study of the nickel concentration in the United States was the result of analyzing air samples collected during 1968–1971 for use in a lead survey (Saltzman et al. 1985). This study is

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significant because numerous sites in four cities were analyzed continuously over 1 year and analyzed by a single, highly experienced laboratory. Samples from 33 sites in Chicago, Houston, New York, and Washington, DC, were analyzed for nickel resulting in respective geometric mean nickel concentrations of 15, 18, 23, and 42 ng/m³. The results for Washington, DC, are in basic agreement with the results obtained from Kowalczyk et al. (1982). In this study, 24-hour samples collected at 10 locations yielded average nickel concentrations ranging from 5.7 to 35 ng/m³, with a mean concentration of 17 ng/m³. The two major contributing sources are believed to be oil and coal combustion. The enrichment factor for nickel over crustal levels in 29 cities is 11 (Gladney et al. 1984). An enrichment factor considerably >1 indicates that the source of an element is anthropogenic. In Houston, the average concentration of nickel in both the fine (0.1–2.5 µm) aerosols and those >2.5 µm was 4±1 ng/m³ (Johnson et al. 1984).

As part of the Airborne Toxic Element and Organic Substances 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 nickel concentrations were 8.0–34.0, 5.0–28.0, 10.0–27.0, and 5.0–13.0 ng/m³ for Camden, Elizabeth, Newark, and Ringwood, respectively. The nickel levels measured in the industrial urban areas may be compared to the arithmetic mean values reported in the National Air Surveillance survey (9.6–11.0 ng/m³) for 1977–1979 (Evans et al. 1984). Summer and winter maxima in the three urban areas ranged from 24.0 to 39.0 and from 81.0 to 112.0 ng/m³, respectively, and 22.0 and 32.0 ng/m³, respectively, for Ringwood.

The first and second highest annual average nickel concentrations in the air in Texas between 1978 and 1982, according to the Texas Air Control Board, were 49 and 34 ng/m³ at Port Arthur and Beaumont, respectively (Wiersema et al. 1984). The statewide 1978–1982 average was 1 ng/m³. Mean nickel levels showed relatively little geographic variation in Ontario where concentrations in southern, central, and northern Ontario were 0.81, 0.91, and 0.58 ng/m³, respectively (Chan et al. 1986).

Nickel concentrations in particulate matter PM₁₀ was measured at three Midwestern sites, two urban sites with a large industrial component and one rural site, in samples collected from September 1985 to June 1988 (Sweet et al. 1993). Nickel concentrations in the fine PM₁₀ particles (<1–2.5 µm) taken from collection sites in East St. Louis and Southeast Chicago averaged 2.1±1.4 (1 SD) and 2.7±2.6 ng/m³, respectively, and were similar to those measured in the coarser PM₁₀ particles (2.5–10 µm) of 1.8±1.5 and 2.1±1.0 ng/m³, respectively. The concentrations of nickel measured in both the fine and coarse particles collected at the East St. Louis and Southeast Chicago sites were higher than the average concentration of

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nickel of 0.5 ± 0.3 and 0.7 ± 0.5 ng/m³ measured in fine and coarse particles, respectively, collected from a rural site (Bondville, Illinois). The higher concentrations of nickel in the East St. Louis and Southeast Chicago sites are attributed to emissions from zinc smelters and steel mills/oil combustion, respectively.

Nickel concentrations in indoor air are generally <10 ng/m³. In a study of 10 homes in the southeast Chicago area, indoor and outdoor air samples were regularly sampled between June 1994 and April 1995 (van Winkle and Scheff 2001). Of the 48 samples taken, 35 had nickel concentrations above the detection limit of the assay with a mean (± 1 SD) concentration of 0.002 ± 0.002 $\mu\text{g}/\text{m}^3$ and a maximum value of 0.008 $\mu\text{g}/\text{m}^3$. The median indoor nickel concentration of 0.003 $\mu\text{g}/\text{m}^3$ was similar to the median outdoor nickel concentration of 0.0034 $\mu\text{g}/\text{m}^3$. Indoor air samples taken from 394 homes in Suffolk and Onondaga Counties of New York State contained nickel concentrations that were similar to those found in the Chicago study (Koutrakis et al. 1992). A mean indoor nickel concentration of 2 ng/m³ (0.002 $\mu\text{g}/\text{m}^3$) was derived from a sampling of 28 homes. The New York study also examined nickel concentrations in indoor air as a function of combustion sources within the home (e.g., resident smoker, wood-burning stove, kerosene heater) and found no difference in the mean nickel concentrations between homes containing these combustion sources and homes without. Graney et al. (2004) measured nickel levels in indoor air as part of a 1998 study of metal exposures for residents of a retirement home in Towson, Maryland. The study participants had a mean age of 84, were all nonsmokers, and did not typically cook their own meals. Median nickel concentrations of 1.02 and 1.71 ng/m³ in air were reported in particulate matter (PM_{2.5}) samples collected from indoor air and personal exposure samplers, respectively. In a study of 46 high school students in New York City conducted in the winter and summer of 1999, the concentrations of nickel in collected particulates (PM_{2.5}) to which these students were exposed was assessed using personal monitoring devices and stationary measurements of airborne nickel both within and outside the home (Kinney et al. 2002). The mean (± 1 SD) air concentrations of nickel obtained from the outdoor, indoor and personal monitors measured during the winter survey period were similar (32.3 ± 22.4 , 31.6 ± 54.5 , and 49.6 ± 114 ng/m³, respectively). Likewise, the mean nickel concentrations obtained from all three monitors during the summer survey period were also found to be similar (11.7 ± 6.3 , 12.6 ± 8.4 , and 17.3 ± 24.7 ng/m³, respectively), although somewhat lower than the winter concentrations. These results suggest that ambient concentrations of nickel are the dominating force in determining both indoor and personal exposures to nickel.

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6.4.2 Water

Surface water contains low nickel levels. Uncontaminated freshwater and seawater typically contain about 300 ng/L of nickel (Barceloux 1999). The concentration in seawater ranges from 100 to 3,000 ng nickel/L. Higher levels are found in deeper waters than in surface water (Mart et al. 1984; Sunderman 1986; van Geen et al. 1988; Yeats 1988). Water from the surface of the Atlantic Ocean, deep within the Atlantic Ocean (400 m), and the Atlantic shelf contained 1.8 nM (106 ng/L), 2.7 nM (158 ng/L), and 3.5 nM (205 ng/L) nickel, respectively (van Geen et al. 1988). Nickel concentration in surface water was found to decrease by a factor of approximately 2 with increases in percent salinity from approximately 30 to 36% and increased with increasing phosphorus concentration (Yeats 1988). Nickel concentrations in South San Francisco Bay were about 3,000 ng/L, with one-third to one-half of the nickel complexed to a class of strong organic ligands (Donat et al. 1994).

The nickel content of fresh surface water has been reported to average between 15 and 20 µg nickel/L (Grandjean 1984; NAS 1975). The concentration of dissolved nickel in the lower Mississippi River ranged from 1.2 to 1.5 µg/L in seven samples taken at different flow conditions (Shiller and Boyle 1987). In a 1977–1979 study of representative groundwaters and surface waters throughout New Jersey, in which >1,000 wells and 600 surface waters were sampled, the median nickel levels in groundwater and surface water were both 3.0 µg/L (Page 1981). The respective 90 percentile and maximum levels were 11 and 600 µg/L for groundwater and 10 and 45 µg/L for surface water. The nature of the sites with elevated nickel levels was not indicated. However, groundwater polluted with nickel compounds from a nickel-plating facility contained as high as 2,500 µg/L (IARC 1990). Nickel concentrations were measured in 30 groundwater samples taken from the South Platte River alluvial aquifer underlying Denver, Colorado (Bruce and McMahon 1996). The samples represented a variety of land-use activities, including commercial, industrial, residential, and agricultural. A median nickel concentration of 3 µg/L was determined, with maximum and minimum concentrations values of 20 and 1 µg/L, respectively.

Nickel concentrations from five stations in Lake Huron in 1980 had median and maximum nickel concentrations of 0.54 and 3.8 µg/L, respectively (Dolan et al. 1986). In a 1982 survey, nickel concentrations in Hamilton Harbor, Lake Ontario, ranged from <1 to 17 µg/L, with a median of 6 µg/L (Poulton 1987). The median nickel concentration from an analogous 1980 survey was 4 µg/L. Suspended sediment in surface samples (0.2 m) at Hamilton Harbor, Lake Ontario, contained 17–23 ppm nickel; samples from a depth of 20 m contained 67–87 ppm, similar to the 66 ppm of nickel found in bottom sediment samples (Poulton 1987). These findings suggest that resuspension of bottom sediment is

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a major contributor to the suspended sediment at 20 m depth. In a 1993 survey of heavy metal concentrations in the Great Lakes, average nickel concentrations of 872 and 752 ng/L were measured in Lakes Erie and Ontario, respectively (Nriagu et al. 1996). Concentrations were highest in near-shore waters due to their proximity to urban centers and polluted river mouths. A decrease in the average concentration of nickel measured in Lake Ontario, from 838 ng/L measured in May/June to a value of 751 ng/L obtained in October, indicates that sedimentation of suspended particles results in a fast depletion of nickel during the summer stratification (Nriagu et al. 1996).

Tap water that is used for drinking purposes generally contains nickel at concentrations ranging from 0.55 to 25 µg/L in the United States (FDA 2000; O'Rourke et al. 1999; Thomas et al. 1999). Nickel concentrations in tap water measured in the Total Diet Study 1991–1999 ranged from 0 to 0.025 mg/kg (\approx 0–25 µg/L) with a mean value of 0.002 mg/kg (\approx 2 µg/L) (FDA 2000). Analysis of data obtained during 1995–1997 from the National Human Exposure Assessment Study (NHEXAS) yielded median concentrations of nickel in tap water (used as drinking water) of 4.3 µg/L (10.6 µg/L, 90% percentile) in the Arizona study and 4.0 µg/L (11 µg/L, 90% percentile) in the EPA Region 5 (Illinois, Indiana, Michigan, Minnesota, Ohio, and Wisconsin) study (O'Rourke et al. 1999; Thomas et al. 1999). In a 1969–1970 survey of 969 water supplies in the United States representing all water supplies in eight metropolitan areas and one state (2,503 samples), 21.7% of samples had concentrations <1 µg/L, 43.2% of the samples contained between 1 and 5 µg nickel/L, 25.6% of the samples contained between 6 and 10 µg nickel/L, 8.5% of the samples contained between 11 and 20 µg nickel/L, and 1% had levels >20 µg nickel/L (NAS 1975).

In a national survey of raw, treated, and distributed water from 71 municipalities across Canada, the median nickel concentration in both treated and distributed provincial drinking water were \leq 0.6–1.3 µg/L for treated water and 1.8 µg/L for distributed water (Meranger et al. 1981). The maximum value was 72.4 µg/L from Sudbury, Ontario. The similarity between median and maximum values for treated and distributed water suggests that nickel is not generally picked up in the distribution system. An exception is in Quebec where the maximum nickel concentration increased from 8.3 to 22.0 µg/L between the treated and distributed water. The median nickel levels in the provincial raw water ranged from \leq 0.6 to 2.3 µg/L. The maximum levels in tap waters from British Columbia, Prince Edward Island, the Yukon, and Northwest Territories were below the detection limit. The similarity in values between raw and treated water indicates that treatment methods (mainly treatment with lime, alum, or soda ash) did not remove nickel effectively.

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Elevated nickel levels may exist in drinking water as a result of the corrosion of nickel-containing alloys used as valves and other components in the water distribution system as well as from nickel-plated or chromium-nickel-plated faucets. In a Seattle study, mean and maximum nickel levels in standing water were 7.0 and 43 $\mu\text{g/L}$, respectively, compared with 2.0 and 28 $\mu\text{g/L}$ in running water (Ohanian 1986). A similar result was observed in a comparison of the mean (± 1 standard deviation) and 90th percentile concentrations of nickel measured during the NHEXAS EPA Region 5 study in standing tap water of (9.2 [± 21] and 16 $\mu\text{g/L}$) and in tap water sampled after the water line had been flushed for 3 minutes (5.3 [± 4.4] and 11 $\mu\text{g/L}$) (Thomas et al. 1999). Even if an individual was to consume only first draw water (containing nickel at the maximum concentration [48 $\mu\text{g/L}$] obtained from the Seattle study) as their sole source of drinking water, their daily intake of 96 $\mu\text{g/day}$ is still less than the lifetime daily limit of 1,400 $\mu\text{g/day}$ (see Table 8-1) set by EPA, assuming a drinking water equivalent level (DWEL) of 700 $\mu\text{g/L}$ and a consumption of 2 L/day (EPA 2000). Although leaching of metals from pipes generally increases with decreasing pH, none of the nickel studies reported the pH of the tap water. First water drawn from hot water taps plated with nickel may contain concentrations as high as 1–1.3 mg/L (Barceloux 1999).

Nickel concentrations were measured as part of a study of heavy metal content in streams and creeks, located in the Black Hills of South Dakota that are impacted by abandoned or active mining operations (May et al. 2001). The concentrations of nickel in these surface waters generally ranged between 1.3 and 7.6 $\mu\text{g/L}$ and were typically highest near where they received drainage water from abandoned or active mining operations. At one location, nickel concentrations as high as 20 $\mu\text{g/L}$ were determined and were attributed to effluent and entrained streambed tailings from previous mining activities. The concentrations of nickel in water did not correlate with the concentrations of nickel in the underlying sediments.

Several investigators reported the presence of nickel concentrations in rain. The annual mean nickel concentration in precipitation at Lewes, Delaware, was 0.79 $\mu\text{g/L}$ (Barrie et al. 1987). The mean concentration (\pm standard deviation) of nickel collected from rain showers in southern Ontario, Canada, in 1982 was 0.56 \pm 0.07 $\mu\text{g/L}$ (Chan et al. 1986). The mean concentrations in northern and central Ontario were both 0.61 $\mu\text{g/L}$, indicating a lack of spatial variability. Sudbury, the site of a large nickel smelter, is located in central Ontario. The nickel concentration in rainwater collected near a large municipal incinerator in Claremont, New Hampshire, was measured at a mean value of 0.69 $\mu\text{g/L}$ (Feng et al. 2000). Nickel concentrations in rain collected between 1985 and 1990 from remote regions of the Atlantic Ocean ranged from 0.63 to 1.42 $\mu\text{g/L}$ (Helmert and Schrems 1995). The concentration of nickel in cloud water

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sampled on the Olympic Peninsula of Washington State in May 1993 was measured at $0.5 \pm 0.4 \mu\text{g/L}$; the air-equivalent concentration is 0.2 ng/m^3 (Vong et al. 1997).

Nickel in snow from Montreal, Canada, was highly enriched compared with ambient air, ranging from 2 to 300 ppb (Landsberger et al. 1983). The nickel content of snow particulate matter was 100–500 ppb. Nickel concentrations were highly correlated with those of vanadium, suggesting that oil combustion was a source. The nickel concentration in snow collected near a large municipal incinerator in Claremont, New Hampshire, was measured at a mean value of $0.62 \mu\text{g/L}$ (Feng et al. 2000). Snow samples were collected several hundred kilometers from the nearest known nickel emission sources (e.g., smelters and ore processing facilities) in northwestern Russia, near the Finish and Norwegian borders. Mean nickel concentrations of 0.0019 mg/L ($1.9 \mu\text{g/L}$) were measured in the snow melt or, based on the volume of accumulated snow, 0.26 mg/m^3 (Kashulin et al. 1997).

6.4.3 Sediment and Soil

Sediment is an important sink for nickel in water. Mean nickel levels in pristine sediment from five sites off the northern coast of Alaska ranged from 25 to 31 ppm (Sweeney and Naidu 1989). Of this amount, $\approx 10\%$ was extractable. Nickel was most highly associated with silt and clay. Background nickel concentrations in sediment cores from open water of Lake St. Clair ranged from 8.5 to 21.1 ppm, with mean concentrations of 13.6 and 17.6 ppm in sand and silty clay sediment, respectively (Rossmann 1988). The average nickel concentrations in surface sediment of four Rocky Mountain lakes ranged from 9.6 to 18 ppm (dry weight). The nickel concentrations of the five other lakes reported in the literature ranged from 6.4 to 38 ppm (Heit et al. 1984). Nickel concentrations measured in the sediments taken in 1998 from the Clark Fork-Pend Oreille and Spokane River Basins in the region adjoined by the states of Washington, Idaho, and Montana ranged from 12 to 27 $\mu\text{g/g}$, dry weight (USGS 2000a).

The range and mean nickel levels in surface sediment of Penobscot Bay, Maine, were 8.22–35.0 and 26.6 ppm (dry weight), respectively (Larsen et al. 1983). This is higher than the levels found at cleaner sites in Casco Bay in the Gulf of Maine (17.6 ppm) and Eastern Long Island (7.6 ppm) (Larsen et al. 1983). As part of the Long Island-New Jersey National Water-Quality Assessment (LINJ-NAWQA) Program, nickel concentrations were measured in bed-sediments taken from streams and rivers in New Jersey in the fall of 1997 (USGS 2000b). A median nickel concentration of $30 \mu\text{g/g}$ (wet weight) was determined in bed-sediments, with values ranging from 18 to 43 $\mu\text{g/g}$. In a similar NAWQA study of the Northern Rockies Intermontane Basins study area, a median nickel concentration in bed-sediments of

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18 µg/g (wet weight) was determined, with a range of values of 12–24 µg/g (USGS 2000a). Rice (1999) gives a summary of trace metal concentrations in 541 bed-sediment samples taken from throughout the conterminous United States as part of the NAWQA study, reporting a median nickel concentration of 27 µg/g, with a larger range of values 6–530 µg/g than found from the results of the separate NAWQA studies noted above. Nickel is more highly associated with fine-grained sediment with a higher organic carbon content. Levels reflect anthropogenic input as well as mineralization of the regional bedrock.

Nickel content in sediments is expected to be high near sources of nickel emissions. For example, nickel carried into creeks and streams from drainage and runoff originating from active or abandoned mining operations in the Black Hills of South Dakota can lead to increased concentrations of this metal in sediments (May et al. 2001). Nickel concentrations varied between 10 and 64 µg/g, dry weight, depending on proximity to nearby mines.

Nickel occurs naturally in the Earth's crust with an average concentration of 0.0086% (86 ppm) (Duke 1980a). The nickel content of soil may vary depending on local geology. A nickel content of 0.5% (5,000 ppm) is common in podzol soil in southeastern United States, and nickel concentrations of >1,000 ppm are not unusual in glacial till in southern Quebec. Both areas are underlain with ultramafic rock, which is rich in nickel. Typical nickel levels reported in soil range from 4 to 80 ppm. In a region north of Sydney, Australia, nickel concentrations as high as 2,030 ppm have been reported in ferrosol topsoils, which are naturally-enriched in nickel through the weathering of underlying haematite, magnetite, quartz, and kaolinite minerals (Lottermoser 2002). A soil survey by the U.S. Geological Survey throughout the United States reported that nickel concentrations ranged from <5 to 700 ppm, with a geometric mean of 13 ± 2.31 ppm, ranking 15th among the 50 elements surveyed (Shacklette and Boerngen 1984). In this survey, samples were taken at 20 cm from 1,318 sampling sites. Cultivated soils contained 5–500 ppm of nickel, with a typical concentration of 50 ppm (Bennett 1984). Nickel concentrations in Canadian soils were generally 5–50 ppm (Webber and Shames 1987). An extensive survey in England and Wales reported that nickel concentrations typically ranged from 4 to 80 ppm, with a median value of 26 ppm (Bennett 1984). The average farm soil in the United States contained >30 ppm nickel (NAS 1975). Mean nickel concentrations in the forest floor from samples collected from 78 sites in nine northeastern states averaged 11 ± 0.8 ppm (Friedland et al. 1986).

Nickel concentrations in contaminated soils within ≈ 8 km of the large nickel smelter at Sudbury, Ontario, ranged from 80 to 5,100 ppm (Duke 1980b). A study of wetland soil-sediment in Sudbury found 9,372 and 5,518 ppm of nickel at sites located 2.0 and 3.1 km from the smelter, respectively (Taylor and

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Crowder 1983). Nickel concentrations declined logarithmically with increasing distance from the smelter. This indicates that nickel accumulations result from atmospheric deposition and soil runoff (Taylor and Crowder 1983). In a more recent survey of nickel content in soils in the Sudbury region, soil samples were taken within 5 km of each of the three smelters located in the area, Copper Cliff, Coniston, and Falconbridge (Adamo et al. 1996). Mean total concentrations of nickel in soil (based on dry weight) of 580, 286, and 210 mg/kg were obtained for the three sites, respectively. Concentration ranges were 80–2149, 156–628, and 23–475 mg/kg for the Copper Cliff, Coniston and Falconbridge sites, respectively.

The concentrations of nickel in soils near another smelting operation have been investigated. At the Pechenganikel Smelter in northwestern Russia, near the border with Norway, deposition rates and soil concentrations of nickel were measured in sampling sites either near the facility or up to 41 km south or southeast of the facility (Koptsik et al. 2003). Nickel deposition rates of >1.75, 0.7, 0.26, and 0.05 mmoles nickel/m²/year (>103, 41, 15, and 3 mg/m²/year, respectively) were determined at distances of 1, 8, 16, and 41 km, respectively, from the smelter. Consistent with the decrease in deposition rates, the concentrations of nickel in soils were also found to decrease from 30 mmoles/kg (1,760 mg/kg) within 1 km of the facility to 9.6 mmoles/kg (560 mg/kg) at 8 km, 6.5 mmoles/kg (380 mg/kg) at 16 km, and 1.0–1.2 mmoles/kg (59–7 mg/kg) at 41 km. The nickel concentrations in soils taken from the farthest sampling site (41 km) are similar to the background concentrations of nickel in soils within the regions that are not influenced by the deposition of nickel from the smelter.

Soils from the Idaho National Engineering Laboratory (INEL) and two background sites in southern Idaho had geometric mean nickel concentrations of 11.8–23.4 ppm dry weight; concentrations are significantly higher near INEL (Rope et al. 1988). The coal-fired steam plant that was constructed at the laboratory in 1982–1983 may be responsible for the higher nickel concentrations.

Nickel concentrations in 57 sludge-treated soils in an agricultural area of Ontario, Canada, ranged from 6.2 to 34 ppm (dry weight), with a mean of 20 ppm (Webber and Shames 1987). For 252 untreated soils, the range and mean values were 4.0–48 and 16.2 ppm, respectively. The mean for sludge-treated soil was significantly elevated.

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6.4.4 Other Environmental Media

There have been several studies regarding nickel content in an average diet. Current information on the dietary intake of nickel in the United States is based on data gathered from the NHEXAS study. Nickel concentrations were measured in duplicate diet samples which, in combination with study participant's estimates of food and water intake, were used to determine both the overall concentration of nickel in combined solids and liquids in the total diet and the average nickel intake of study participants. In the EPA Region 5 (Illinois, Indiana, Michigan, Minnesota, Ohio, and Wisconsin) study, the mean and median concentrations of nickel in combined dietary solids and liquids were 47 and 43 $\mu\text{g}/\text{kg}$, respectively (Thomas et al. 1999).

In other studies of nickel in the diet, Myron et al. (1978) analyzed nine institutional diets consisting of three meals each. Four of these meals were sampled from the student center at the University of North Dakota. The remaining five diets were special diets from a rehabilitation hospital. The average nickel concentration and nickel content of the student meals ranged from 0.19 to 0.29 ppm and from 140 to 221 μg , respectively. For the hospital meals, the nickel concentration ranged from 0.21 ppm (107 μg) in the puree meals to 0.41 ppm (176 μg) in the low-calorie meal. Breakfast had the lowest nickel content. The average daily dietary nickel intake for the nine diets was 168 ± 11 μg . The average nickel concentration in the food was 0.27 ppm (dry weight). These results are comparable with estimated daily intakes of nickel of 150 μg in Denmark, 73–142 μg in Switzerland, and 140–150 μg in the United Kingdom (IARC 1990; Nielsen and Flyvholm 1984). A 1962 study that used the nickel content of individual foods to estimate average dietary nickel intake reported intakes of 300–600 μg , which are much higher than those reported above (Grandjean 1984).

The foods with the highest mean nickel content were oatmeal, spinach, asparagus, and peas (IARC 1990). Nuts and cocoa may have nickel levels as high as 3 and 10 ppm, respectively. In a market basket survey completed in the United States (Pennington and Jones 1987), the highest average levels of nickel in $\mu\text{g}/100$ g were found in nuts (128.2), legumes (55), sweeteners (31.6), grains and grain products (26.2), and mixed dishes and soups (25.3). From data gathered in the FDA Total Diet Study 1991–1996, the mean and median nickel concentrations in the food items that were surveyed were 0.136 and 0.057 mg/kg, respectively (Capar and Cunningham 2000). The highest concentrations of nickel were found in mixed nuts (3.04 mg/kg), oat ring cereal (2.32 mg/kg), chocolate syrup (1.04 mg/kg), granola cereal (1.01 mg/kg), and peanuts (0.956 mg/kg). Other products with notable nickel concentrations are legumes and nuts (0.368–3.04 mg/kg), cereals containing largely whole wheat, corn, oats, or rice (0.216–

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2.32 mg/kg), chocolate products (0.19–1.04 mg/kg), and canned peaches and pineapple juice (0.408–0.668 mg/kg). In an analysis of trace metals in tissue samples taken from livestock and poultry, mean nickel concentrations were 0.23–0.82 ppm in muscle, 0.23–0.29 ppm in liver, and 0.28–0.57 ppm in kidneys (Coleman et al. 1992).

A Canadian survey of nickel in infant formulas gave a median value of 3.53 µg/L for evaporated milk (Dabeka 1989). Different types of milk-based formulas contained from 5.8 to 28.9 µg nickel/L (Dabeka 1989). All concentrations are on a ready-to-use basis. Formulas fortified with iron had a higher nickel content. The median nickel content of soy-based formula ranged from 31.2 to 187 µg nickel/L. The average daily dietary intake of nickel by infants between the ages of 0 and 12 months could vary from 35.7 µg (4.5 µg/kg) (if evaporated milk was fed) to 74.7 µg (10.2 µg/kg) (if concentrated liquid soy-based formula was used). Infant formula (base not stated) in the United States contained an average of 0.2 µg nickel/100 g (Pennington and Jones 1987).

There is limited evidence that stainless steel pots and utensils may release nickel into acid solution (IARC 1990). Six stainless steel pots of different origins were tested to see whether they would release nickel by boiling 350 mL of 5% acetic acid in them for 5 minutes (Kuligowski and Halperin 1992). The resulting concentrations of nickel ranged from 0.01 to 0.21 ppm. Cooking acidic fruits in new stainless steel pans resulted in an increase of nickel that was about one-fifth the average daily nickel intake (Flint and Packirisamy 1995). Further use of the pans did not result in any release of nickel into the food. The use of nickel-containing catalysts in the hydrogenation of food fats may contribute to elevated nickel levels in food (Mastromatteo 1986). Grain milling may also lead to higher nickel levels (IARC 1990). The results from a recent study that attempted to identify the influence of the container on the trace metal content of preserved pork products showed no clear evidence that the metal container contributed to the metal content of the food (Brito et al. 1990). The nickel concentration was highest in products in china and glass containers, rather than those in metal and plastic containers.

The nickel content of cigarettes is 1–3 µg; ≈10–20% of this nickel is released in mainstream smoke (Sunderman 1986). This indicates that 2–12 µg of nickel are inhaled for each pack of cigarettes smoked. Torjussen et al. (2003) reported a mean nickel concentration of 0.03 µg/g in smoke condensate isolated from the control combustion of five packets of cigarettes representing five U.S. brands. This compares to mean concentrations of nickel of 1.72 and 1.57 µg/g in the tobacco and ash, respectively. Most of the nickel is in the gaseous phase, but the chemical form of the nickel is unknown (IARC 1990).

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In a comprehensive survey of heavy metals in sewage sludge, 31 sludges from 23 American cities were analyzed by electrothermal atomic absorption spectroscopy (AAS) (Mumma et al. 1984). The nickel concentration in the sludges ranged from 29.0 to 800 ppm (dry weight) and had a median value of 195 ppm. The highest concentration of nickel in sludge was in Detroit, Michigan. For comparison, the concentration of nickel in cow manure was 28.0 ppm. In another study of heavy metal in sludges generated at waste water treatment plants in 16 large U.S. cities, nickel concentrations (dry weight) were found to range from 18 to 186 ppm, with a median value of 66.8 ppm (Gutemann et al. 1994).

Nickel was detected in a large number of the 283 point samples taken from leachate collected from 48 codisposal, hazardous, or municipal solid waste (MSW) sites (Gibbons et al. 1999). Codisposal sites were defined as those facilities accepting municipal wastes and relatively large volumes of industrial sludges, liquids, and solids. Dissolved nickel was detected in 43 of 45 codisposal sites, all 48 old (accepting waste before 1986) hazardous waste sites, all 29 old (accepting waste before 1984) MSW sites, and 1 of 1 new (accepting waste after 1984) MSW site. Solid nickel was detected in 105 of 111 codisposal sites, 108 of 126 old (accepting waste before 1986) hazardous waste sites, 108 of 116 old (accepting waste before 1984) MSW sites, and 36 of 43 new (accepting waste after 1984) MSW sites.

Mosses are used to monitor atmospheric deposition of metals. The metals measured in mosses are obtained only from the passive uptake of metals that are deposited onto the organism from the air. In a study of heavy metal concentrations measured mainly in *Pleurozium schreberi* taken from 16 regions in West Germany and the former German Democratic Republic (GDR), a decrease in the mean nickel concentration occurred in moss samples taken in 1990–1991 (2.3 µg/g) and 1995–1996 (1.63 µg/g) (Herpin et al. 2004). This decrease follows a decrease in the total airborne emissions of nickel in Germany from 277 to 159 tons/year.

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Nickel occurs naturally in the Earth's crust, and the general population will be exposed to low levels of nickel in ambient air, water, and food. Based on several dietary studies, the average daily dietary intake of nickel in food ranges between 69 and 162 µg/day (NAS 2002; O'Rourke et al. 1999; Pennington and Jones 1987; Thomas et al. 1999). In a more recent total dietary study (NAS 2002), the mean daily dietary intake of nickel ranged from 101 to 162 µg/day for individuals >18 years of age with males ranging from 136 to 140 µg/day and females ranging from 107 to 109 µg/day. Pregnant females averaged a daily dietary intake of 121 µg/day, whereas lactating females averaged 162 µg/day. Also, based on data

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obtained from the National Health and Examination Survey III (NHANES III), it has been estimated that approximately 5 µg/day of the daily dietary intake of nickel comes from dietary supplements (NAS 2002). The daily intake from drinking water is ≈8 µg, assuming a median nickel concentration of ≈4 µg/L and a consumption rate of 2 L water/day. For the highest municipal level in drinking water, which is 68 µg/L in Sudbury, Ontario, the average daily intake of nickel would be 140 µg. Assuming that a person inhales 20 m³ air/day and the average nickel concentration in ambient air in the United States is 2.22 ng/m³, the average nickel intake by inhalation would be 0.0444 µg/day. Based on the highest ambient nickel levels reported for the Copper Cliff (6,100 ng/m³) and Sudbury basin region (732 ng/m³) in Ontario (CEPA 1994), the daily inhalation intake for individual living in these areas could have been as high as 122 and 15 µg/day, respectively. However, based on the mean ambient nickel concentrations measured in Sudbury area of 21 ng/m³ (CEPA 1994) the daily nickel the average daily nickel intake is estimated to be 0.42 µg/day. The nickel intake via inhalation is, therefore, a minor source of nickel to the general, nonsmoking population.

A market basket survey in England completed in 1984 estimated a dietary intake of 154–166 µg/day or 2.2–2.4 µg/kg/day for a 70-kg person (Smart and Sherlock 1987). Dietary intake of nickel in the United States has been estimated to range from 69 µg/day for 6–11-month-old infants to 162 µg/day for teenage boys, with a level of 146.2 µg/day or 2 µg/kg/day for a 25–30-year-old male weighing 70 kg (Pennington and Jones 1987). More recent data on nickel intakes from the U.S. diet come from the results of the NHEXAS studies. Mean and median dietary intakes of nickel for study participants in the EPA Region 5 study were calculated to be 2.2 and 1.4 µg/kg body weight/day, respectively, or 154 and 98 µg/day for a 70-kg adult, respectively (Thomas et al. 1999). O'Rourke et al. (1999) have taken the dietary nickel data obtained from the Arizona study and determined the dietary nickel intake for various subpopulations (Table 6-3). The mean daily nickel intake for all subjects was 153 µg/day, with the highest mean intake for an adult male (163 µg/day) and lowest intake for children (125 µg/day). Hispanic study participants were found to have a lower mean dietary intake (141 µg/day) than non-Hispanic participants (155 µg/day). Total nickel intake for Canadians in the general population has been estimated to range from 4.4 to 22.1 µg/kg/day, with greater intake estimated for infants than for adults (CEPA 1994). Food, from which nickel is poorly absorbed, accounted for most of the intake (4.4–22 µg/kg/day). It was estimated that cigarette smoking may increase total daily intake by 0.12–0.15 µg/kg/day. Living in the vicinity of Sudbury, Ontario, where large nickel deposits are found, water intake of nickel for individuals aged 12 years old or older ranged from 0.6–2.5 µg/kg/day. However, the estimated water intake of nickel increased with decreasing age of the study group, for example 0.87–3.6 µg/kg/day for children ages 5–11 years old to 2.8–12 µg/kg/day for newborns and infants under the age of 0.5 years.

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Table 6-3. Total Dietary Exposure Estimates of Study Participants to Nickel Based on the Dietary Information Obtained from the NHEXAS Arizona Study^a

Exposure population	Number of participants evaluated	Daily nickel intake (μg)		
		Mean intake	Median intake	Range
All subjects	176	153	135	27–562
Adult male (>18 years of age)	55	163	145	38–372
Adult female (>18 years of age)	86	157	135	23–563
Children (<18 years of age) ^b	35	125	107	31–343
Hispanic	54	141	134	27–401
Non-Hispanic	119	155	132	42–563

^aO'Rourke et al. 1999

^bEither gender

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In another approach to determining daily nickel intake within subpopulations in the United States, Moschandreas et al. (2002) used the Dietary Exposure Potential Model (DEPM) and data obtained from Combined National Residue Database (CNRD) to estimate dietary nickel intake based on food consumption patterns in subpopulations and nickel content in specific food items. The food items used in the model are based on 11 food groups consisting of approximately 800 exposure core foods that represent 6,500 common food items. The results of their model (Table 6-4) yielded an average dietary nickel intake in the U.S. population of 0.374 $\mu\text{g}/\text{kg}$ body weight/day, or 26.2 $\mu\text{g}/\text{day}$ for a 70-kg adult. Their results also indicate that children under the age of 7 have a nickel intake that is at least 1.8 times higher than the average for the overall population. However, the estimates obtained for dietary nickel intake from the DEPM model are lower than the daily nickel intakes determined from the NHEXAS study (Table 6-3). Moschandreas et al. (2002) attribute these differences in intake values for nickel to differences in study populations, methods for assigning values to measurements that are below the level of detection, and potential errors in recording portion sizes in the NHEXAS study.

The general population is also exposed to nickel in nickel alloys and nickel-plated materials including steel, coins, and jewelry (Barceloux 1999). Jewelry and other items made of silver may either contain, or be coated with, nickel to reduce oxidation. White gold contains 10–15% nickel and some gold-plated items may have a nickel undercoating. Residual nickel may be present in soaps, fats, and oils hydrogenated with nickel catalysts (Sunderman 1986). In U.S. coinage, the 5-cent coin is composed of a cupronickel alloy containing 25% nickel and 75% copper, whereas only the faces of the 10-cent, quarter-dollar, half-dollar, and 1 dollar coins contain the cupronickel alloy (United States Treasury 2004). Studies of European coins, especially the recently introduced Euro coinage, show the transfer of nickel from coins to hands (Fournier and Govers 2003). For example, as part of a 58-coin counting exercise, it was determined that an average of 0.23 μg of nickel was transferred to three fingers during a 2–3-second manipulation of an unwashed Euro coin that had been in circulation for 2–5 months.

A NOES survey conducted by NIOSH from 1981 to 1983 estimated that 727,240 workers are potentially exposed to nickel metal, alloys, dust, fumes, salts, or inorganic nickel compounds in the United States (NIOSH 1990). Seventy percent of these estimated exposures are to nickel of an unknown molecular formula. The numbers of workers estimated to be exposed to nickel chloride, nickel oxide, and nickel sulfate are 48,717, 18,166, and 56,844, respectively. The estimate is provisional because all of the data for trade name products that may contain nickel have not been analyzed. The NOES was based on field surveys of 4,490 businesses employing nearly 1.8 million workers and was designed as a nationwide survey based on a statistical sample of virtually all workplace environments in the United States where

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Table 6-4. Dietary Exposure Estimates of U.S. Populations to Nickel Based on the Dietary Exposure Potential Model (DEPM)^a

Subpopulation	Nickel intake (µg/kg body weight/day)
U.S. population	0.374
Age/gender	
Nonnursing infants	0.870 ^b
Children 1–6	0.669
Children 7–12	0.425
Females 13–19	0.281
Females 20+	0.350
Females 55+	0.368
Males 13–19	0.324
Males 20+	0.342
Males 55+	0.369
Ethnicity	
Hispanic	0.407
Non-Hispanic white	0.424 ^b
Non-Hispanic black	0.295
Non-Hispanic other	0.258
Geographic region ^c	
North central	0.238
Northeast	0.379
Southern	0.359
Western	0.423 ^b
Family income ^d	
Poverty 0–130%	0.420 ^b
Poverty 131%+	0.362

^aMoschandreas et al. 2002

^bValues indicate the maximum exposure to nickel for each subpopulation group.

^cThe regional classification is as defined by the U.S. Department of Agriculture, and is based upon U.S. Census Bureau regions.

^dAnnual household income as a percentage of the Poverty Index.

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eight or more persons are employed in all standard industrial codes except mining or agriculture. Industries with especially large numbers of potentially exposed workers include the following: plumbing, heating, air conditioning, pressed and blown glass, steel, plating and polishing, aircraft, shipbuilding, railroad, control and measuring instruments, and repair services (NIOSH 1990).

Occupational exposure to nickel will be highest for those involved in production, processing, and use of nickel. There are currently no people in the United States employed in nickel mines, smelters, and refineries at the end of 2001. Primary nickel production in the United States ceased for several years in the late 1980s (Kirk 1988a). The mining and smelting operation in Riddle, Oregon, was reactivated in 1989–1990, and was decommissioned in 2001 (Kuck 2002). The concentration range of airborne nickel that workers were exposed to in laterite mining and smelting in Riddle, Oregon, was 4–420 $\mu\text{g}/\text{m}^3$ (Warner 1984). The ranges of airborne nickel concentrations reported for other industries are as follows: stainless steel production, <1–189 $\mu\text{g}/\text{m}^3$; high nickel alloy production, 1–4.4 $\mu\text{g}/\text{m}^3$; foundry operations, from not detectable to 900 $\mu\text{g}/\text{m}^3$; electroplating, <2–<16 $\mu\text{g}/\text{m}^3$; nickel-cadmium battery manufacture, 20–1,910 $\mu\text{g}/\text{m}^3$; nickel catalyst production from nickel sulfate, 1–1,240 $\mu\text{g}/\text{m}^3$; production of nickel salts from nickel or nickel oxide, 9–590 $\mu\text{g}/\text{m}^3$; and production of wrought nickel and alloys from metal powder, 1–60,000 $\mu\text{g}/\text{m}^3$ (Anttila et al. 1998; Haber et al. 2000; Magari et al. 2002; Seilkop and Oller 2003; Warner 1984). The average nickel concentration for selected work areas or operations in these industries, other than producing wrought nickel and alloys from metal powder, is <3–378 $\mu\text{g}/\text{m}^3$; for wrought nickel and alloy production from metal powder, the average concentration is 1,500 $\mu\text{g}/\text{m}^3$.

Operations that produce the highest levels of airborne nickel are those that involve grinding, welding, and handling powders. In a survey of 20 individuals involved in the welding or grinding of stainless steel components, nickel concentrations of 0.340–10.129 mg/m^3 were measured in the workplace atmosphere (Borská et al. 2003). Not only do occupational exposures vary widely among these operations and industries, but also the form of nickel that workers are exposed to varies as is exemplified in Table 6-5. In another example, Berge and Skyberg (2003) determined the exposure factors and species of nickel for 1,046 nickel refinery workers. Mean exposures factors (range of values) of 5.59 $\text{mg}/\text{m}^3/\text{year}$ (0–101.38 $\text{mg}/\text{m}^3/\text{year}$), 1.43 $\text{mg}/\text{m}^3/\text{year}$ (0–24.27 $\text{mg}/\text{m}^3/\text{year}$), 0.55 $\text{mg}/\text{m}^3/\text{year}$ (0–15.21 $\text{mg}/\text{m}^3/\text{year}$), 0.52 $\text{mg}/\text{m}^3/\text{year}$ (0–14.61 $\text{mg}/\text{m}^3/\text{year}$), and 3.09 $\text{mg}/\text{m}^3/\text{year}$ (0–72.99 $\text{mg}/\text{m}^3/\text{year}$) were determined for total nickel, soluble nickel, sulfidic nickel, metallic nickel and oxidic nickel, respectively. Because sulfur has a deleterious effect on many metals and alloys, nickel sulfate and sulfidic nickel compounds are generally not found in metallurgical workplaces (Warner 1984). Nickel subsulfide is known to exist in only one application in nickel-using industries, namely in certain spent catalysts. Nickel oxide is used as

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Table 6-5. Nickel Levels in Air and Distribution of Different Forms of Nickel as a Proportion (by Weight) of Total Nickel in Selected Departments and Time Periods at a Nickel Refinery in Norway^a

Department and period	Total nickel in air (mg/m ³)	Proportion of total nickel			
		Soluble nickel	Sulfidic nickel	Metallic nickel	Oxidic nickel
Crushing and grinding					
1990–1994	0.7–1.4	0.12	0.72	0.11	0.04
Smelter					
1910–1929	4.0	0.10	0.05	0.01	0.84
1930–1950	4.0	0.10	0.05	0.08	0.77
1951–1977	2.6–4.4	0.10	0.04	0.18	0.68
Calcining, smelting					
1951–1977	1.5–3.4	0.10	0.05	0.01	0.84
1978–1994	0.5	0.12	0.13	0.01	0.74
Roasting					
1910–1977	1.9–5.3	0.10	0.15	0.03	0.72
1978–1994	0.4	0.15	0.05	0.00	0.80
Copper leaching					
1910–1994	0.1–1.5	0.49	0.01	0.01	0.49
Copper electrolysis					
1910–1994	0.03–0.2	0.80	0.04	0.04	0.13
Copper cementation					
1927–1977	0.6–1.2	0.45	0.05	0.45	0.05
Electrolytic purification					
1927–1977	0.2–0.5	0.80	0.03	0.15	0.02
1978–1994	0.03–0.2	0.98	0.01	0.00	0.01
Nickel electrolysis					
1910–1977	0.1–0.2	0.87	0.05	0.01	0.08
1978–1994	0.03–0.1	0.83	0.04	0.02	0.11

^aGrimsrud et al. 2002

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a raw material in steel production, and oxide fumes and dust may occur in melting, casting, and welding operations. There are probably more exposures to metallic nickel in nickel-using industries than in nickel-producing industries. These occur during powder handling, grinding, and polishing operations and in casting operations.

Nickel is an essential trace element for animals (Sunderman 1986), and a 70-kg reference man contains 10 mg of nickel, giving an average body concentration of 0.1 ppm (Iyengar 1986). The highest tissue concentrations of nickel are found in the lungs of nickel smelting and refinery workers. The highest nickel concentration reported in lung tissue of 39 nickel refinery workers autopsied in 1978–1984 was 1,344 ppm (dry weight), compared to 1.7 ppm in unexposed persons (Andersen and Svenes 1989). In another study of nickel content in the lungs of 15 former nickel refinery workers, the arithmetic mean (± 1 SD) for nickel concentrations in workers was 50 ± 150 $\mu\text{g/g}$, dry weight, in comparison to a value of 0.74 ± 0.44 $\mu\text{g/g}$ in 10 individuals not connected to the refinery industry (Svenes and Anderson 1998). In a multi-element analysis of lung tissue obtained from former nickel refinery workers who were retired for 10–15 years, it was found that one form of nickel remained in the lung following 15–20 years of the occupational exposure (Andersen and Svenes 2003). The remaining nickel is contained within an inhaled mineral, trevorite, which is water-insoluble. The concentration of nickel in the lung tissue within one donor varied from 3.0 to 64.1 $\mu\text{g/g}$ dry weight, depending on the sampling site within the lung.

Ten studies of nickel in human milk gave disparate results. Six median values ranged from 5 to 16 $\mu\text{g/L}$, and 10 mean values ranged from 1.5 to 39 $\mu\text{g/L}$ (Iyengar 1989). Five of the six medians ranged from 11 to 16 $\mu\text{g/L}$. The lowest and highest mean values were from Finland and Germany GDR, respectively. Biego et al. (1998) were not able to detect nickel in breast milk above the detection limit of 2.9 $\mu\text{g/L}$ of the assay. However, mean (± 1 SD) nickel concentrations were determined for formula (30 ± 3 $\mu\text{g/L}$) and soya milk (450 ± 220 $\mu\text{g/L}$). Individual values ranged from not detectable to 130 μg nickel/L. In one study from the United States, the nickel concentrations in human breast milk were measured between 1 and 38 days postpartum (Casey and Neville 1987). The concentrations ranged from 0.52 to 2.04 ng/mL with a mean value of 1.16 ng/mL. There was no significant change in the values as a function of time postpartum.

Nickel concentrations in human serum taken from 30 individuals not occupationally exposed to nickel ranged from <0.05 to 1.05 $\mu\text{g/L}$ with a mean value of 0.34 $\mu\text{g/L}$ (Barceloux 1999). In another example, nickel concentrations in serum obtained from individuals without occupational exposures to nickel ranged from 0.18 to 0.54 $\mu\text{g/L}$ with an average of 0.36 $\mu\text{g/L}$ (Christensen 1995). Serum nickel levels in hospital

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workers averaged 0.6 ± 0.3 $\mu\text{g/L}$ in Sudbury, Ontario, versus 0.2 ± 0.2 $\mu\text{g/L}$ in Hartford, Connecticut (Hopfer et al. 1989). Measurements of nickel content of tap water in these communities were reported as 109 ± 46 and 0.4 ± 0.2 $\mu\text{g/L}$, respectively (Hopfer et al. 1989). A mean nickel concentration of 4.80 ± 2.69 $\mu\text{g/L}$ was measured in urine samples collected for the NHEXAS Arizona study (EPA 2003t). Concentrations of nickel in the blood and urine of workers at a rolling mill in Poland were 18.5 ± 4.0 and 25.7 ± 5.1 $\mu\text{g/L}$, respectively (Baranowska-Dutkiewicz et al. 1992). Mean concentrations of nickel in urine of individuals not occupationally exposed to nickel are generally < 2 $\mu\text{g/L}$ and can range as high as 9–10 $\mu\text{g/L}$ (95% upper confidence limit) in healthy adults (Barceloux 1999). Workers at a galvanizing plant in Brazil exposed to airborne nickel sulfate at concentrations of 2.8–116.7 $\mu\text{g/m}^3$ had nickel concentrations in their urine ranging between 2.1 and 58.7 $\mu\text{g/g}$ creatinine (2.3–54.9 $\mu\text{g Ni/L}$) with mean values of 8.7 ± 7.8 and 14.7 ± 13.5 $\mu\text{g/g}$ creatinine (10.5 ± 7.5 and 20.6 ± 18.1 $\mu\text{g Ni/L}$) in preshift and postshift samples, respectively (Oliveira et al. 2000). Mean concentrations of nickel in the urine of the control group (workers in a zinc plating plant) were 3.7 ± 2.5 $\mu\text{g/g}$ creatinine or 4.9 ± 2.2 $\mu\text{g/L}$. Danadevi et al. (2003) reported a high mean nickel concentration in the urine obtained from 57 welders of 131.0 $\mu\text{g/L}$ (standard deviation of ± 52.6 $\mu\text{g/L}$) compared to a mean concentration of 17.4 $\mu\text{g/L}$ (standard deviation of ± 8.9 $\mu\text{g/L}$) in urine taken from control individuals who were not occupationally exposed to nickel. However, airborne concentrations of nickel were not reported in this study. Nickel concentrations in the urine of preschool children in Poland were 10.6 ± 4.1 and 9.4 ± 4.7 $\mu\text{g/L}$ for children from an industrial region and a health resort, respectively (Baranowska-Dutkiewicz et al. 1992). After reviewing studies of nickel concentrations in humans, Templeton et al. (1994) indicated that the most reliable reference values were 0.2 $\mu\text{g/L}$ for nickel in serum of healthy adults and 1–3 $\mu\text{g/L}$ for nickel in urine. These values are dependent on food and fluid intake and environmental factors. Fewer studies of nickel in whole blood were identified, and a reference value was not suggested.

Fingernail samples from 71 Americans contained 0.57 ppm of nickel; samples from residents of Japan, India, Canada, and Poland had nickel concentrations that ranged from 1.1 to 3.9 ppm (Takagi et al. 1988). Nickel levels are higher in males than in females. Higher levels occur in younger people and decrease with age. The mean concentration of nickel in hair samples from 55 men and women from Scranton, Pennsylvania, was 1.01 ppm; populations from cities in Japan, India, Canada, and Poland had mean nickel levels between 0.26 and 2.70 ppm (Takagi et al. 1986). A more recent National Health and Nutritional Examination Survey II of hair from a random sample of 271 adults, ages 20–71, from three communities had geometric mean and median nickel levels of 0.39 and 0.45 ppm, respectively. Ten percent of the group had nickel levels > 1.50 ppm (DiPietro et al. 1989).

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The nickel content of most natural vegetation is 0.05–5 ppm on a dry weight basis (NAS 1975). Near source areas, nickel on plants may be elevated because of direct foliar deposition. Some species of plants have the ability to hyperaccumulate nickel (Brooks 1980). The concentration in the leaves of *Alyssum bertolonii* contained 120 ppm nickel. These plants are thought to produce organic ligands that complex with nickel.

The modal concentration of nickel in 159 species of edible fin fish from the U.S. National Marine Fisheries Survey was 0.2–0.3 ppm (wet weight) (Heit et al. 1989). Jenkins (1980) has compiled literature concentrations of nickel levels in aquatic species. The ranges of nickel concentrations in freshwater fish, marine fish, and mollusks from areas thought to be uncontaminated are from <0.2 to 2.0, from not detectable to 4.0, and from 0.4 to 2.0 ppm (wet weight), respectively. The highest levels found near sources of pollution, especially near nickel smelters, were 51.6 ppm for freshwater fish and 191.0 ppm for mollusks. The nickel content of muscle tissue of several fish species collected from metal-contaminated lakes near Sudbury, Ontario, was below the detection limit (2.0 ppm dry weight), except for two of four yellow perch, which had levels of 2.8 and 3.4 ppm (Bradley and Morris 1986). A more recent survey of metals in stocked lake trout in five lakes near Sudbury, Ontario, reported that concentrations of metal in trout muscle were not significantly different from those in the hatchery (0.34–0.83 ppm wet weight versus 0.49 ppm) (Bowlby et al. 1988). Nickel concentrations in the lower Savannah River and Savannah National Wildlife Refuge in Georgia were higher than those reported above for uncontaminated areas. These levels were consistently higher in gar (2.35–6.67 ppm wet weight) than in catfish (0.371.41 ppm) (Winger et al. 1990). Nickel could not be measured above the detection limit (0.5 µg/g, dry weight) in livers taken from lesser scaup collected along the Mississippi Flyway between Manitoba and Louisiana (Custer et al. 2003). As part of the National Status and Trends Program for Marine Environmental Quality, the concentration of nickel in oysters and mussels was investigated (NOAA 1987). The nickel concentration in bivalve tissue collected in 1986 ranged from 0.55 to 12.57 ppm (dry weight). The highest tissue concentration was found in Matagorda Bay, Texas, and the second highest concentration, 6.57 ppm, was found in both Tomales Bay, California, and Chesapeake Bay, Maryland. Oysters around three coastal marinas in South Carolina with sediment nickel levels of 25.8–40.8 ppm (dry weight) had levels of 0.35.2 ppm (Marcus and Thompson 1986). Mean nickel levels in oysters at four sites in the Mississippi Sound varied from <0.5 to 4.7 ppm (wet weight) (Lytle and Lytle 1990).

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6.6 EXPOSURES OF CHILDREN

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

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Exposures of children to airborne nickel are expected to be similar to those found for adults. However, differences in the exposure to nickel contained in deposited particulates (e.g., household dust) are expected to be higher in children, due to greater contact of children with floors and other surfaces, in addition to greater oral and dermal contact with these deposited particulates through the mouthing of toys, hands, feet, etc. Concentrations of nickel in dust collected from homes in Ottawa, Ontario, averaged 62.9 mg/kg with values as high as 116.4 mg/kg (Butte and Heinzow 2002). However, it is not known how much nickel a child absorbs through oral or dermal contact with household dust.

Nickel that is dissolved in water is expected to be a minor exposure route for children, due to the generally low concentrations of nickel in drinking water and groundwater (Sections 6.4.2 and 6.5). However, in areas near nickel smelters and refineries where source water used to produce drinking water is contaminated with nickel, intake of nickel through drinking water for individuals in the affected area will be elevated above that for individuals in the surrounding region whose drinking water is unaffected by these sources of nickel contamination, but is expected to be less than nickel intake through food. Exposure to nickel through consumption of human breast milk is expected to be comparable to or lower than milk-based and soy-based formulas, based on the similar concentration ranges of nickel in these fluids (Biego et al. 1998; Dabeka 1989; FDA 2000; Iyengar 1989). Based on the data from Casey and Neville (1987), the intake of nickel through consumption of breast milk averages 0.8 µg/day between the ages of 4 and 38 days postpartum. For 3-month-old children, it is estimated that daily intake of nickel through the consumption of breast, bottled, dried, and evaporated milk is below 2 µg/day (Biego et al.

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1998). However, daily intake could be higher when consuming some formulas and soya milk, with estimates as high as 21 and 315 $\mu\text{g}/\text{day}$, respectively, being reported (Biego et al. 1998).

Another source of nickel exposure in children is through soil. Children generally receive higher exposure to soil contaminants per unit body weight than adults (Lottermoser 2002). Small children have large surface-to-mass ratios, which provide a greater potential to transdermally absorbed compounds, especially for children crawling in dirt. Also, the skin of newborns and children is more permeable than adult skin. Nickel in an ionized form, such as nickel salts, penetrates intact skin at a slow rate and can also be absorbed at sites of injury to skin (Barceloux 1999). However, nickel exposure through dermal exposure is minimal compared to exposures to nickel through ingestion of soil. The population at greatest risk are children between the ages of 2 and 3 years old as a result of hand-to-mouth activities and those with soil-eating disorders (Lottermoser 2002). A child's intake of nickel through ingestion of soil could be especially important in areas where soils that are naturally enriched with nickel (for example, some soils in the southeastern United States, southern Ontario, or eastern Australia) or have been contaminated with nickel (for example in the Sudbury, Ontario, region) (Section 6.4.3). However, due to the limited bioavailability of nickel in some soils, the amount of nickel that a child actually absorbs from ingested soils could be rather limited. For example, ingestion of 100 mg of ferrosol soil containing 149 mg nickel per kg of soil is calculated to contribute an intake of 0.000149 mg nickel/day, assuming a relative bioavailability for nickel of 1% (Lottermoser 2002).

The primary route of nickel exposure in children is expected to be through the diet. Measurements of nickel in duplicate diet samples obtained from the EPA Region 5 studies indicates that average nickel concentration in combined solids and liquids of 47 $\mu\text{g}/\text{kg}$, which is higher than the average nickel concentration in drinking water of approximately 5 $\mu\text{g}/\text{kg}$ (5.3 $\mu\text{g}/\text{L}$) (Thomas et al. 1999). Using the portion size information recorded by study participants in the NHEXAS Arizona study, daily dietary intakes of nickel for children (<18 years of age) have been calculated to range from 31 to 343 μg , with a mean value of 125 μg (O'Rourke et al. 1999). These intake levels were lower than the average dietary nickel intake of 153 $\mu\text{g}/\text{day}$ calculated for the overall study population (Table 6-3). Likewise, in another total dietary study taken between 1991 and 1997 the mean daily dietary intake of nickel in food of 9–99 $\mu\text{g}/\text{day}$ for children under the age of 9 years was also found to be lower than the mean intake derived for the total study population of 114 $\mu\text{g}/\text{day}$ (NAS 2002). Mean daily nickel intakes of 9, 39, 82, and 99 $\mu\text{g}/\text{day}$ were determined for children aged 0–6 months, 7–12 months, 1–3 years, and 4–8 years, respectively. Nevertheless, the ranges in the mean daily dietary intakes of nickel in children aged 9–18 years (128–137 $\mu\text{g}/\text{day}$ in males and 101–109 $\mu\text{g}/\text{day}$ for females) are similar to the mean intakes

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determined in adults (>18 years of age) (see Section 6.5). Information on dietary nickel intake for non-nursing children and children ages 1–6 (Table 6-4) obtained from DEPM model (Moschandreas et al. 2002) indicates that these children have a higher intake of nickel than the average intake for the U.S. population. Even so, the daily intake of nickel in these children is estimated (4–13 µg/day based on 6–20 kg total body weight) to be much lower than the average dietary nickel intake (125 µg/day) obtained from the NHEXAS study. Also, results from a study of dietary nickel in 2-year-old children in the United Kingdom, where an average daily intake of 81 µg/day (range of 14–260 µg/day) was estimated from the weekly nickel intake of 0.57 mg of nickel (range of 0.1–1.8 mg) given in the reference (Smart et al. 1987), would suggest a higher daily nickel intake in young children than is indicated based on the results of the DEPM model.

For infants who are exclusively breastfed, the daily intake of nickel is estimated to be approximately 1 µg/day (NAS 2002). This estimate is based on a concentration of mean nickel concentration of 1.2 ng/mL in breast milk and an average secretion of 0.78 L/day.

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In discussing nickel exposure, it is important to consider what form of nickel a person is exposed to and its bioavailability. Such information is not often available. Although high concentrations of nickel may be found in contaminated soil and sediment, it may be embedded in a crystalline matrix or bound to hydrated iron, aluminum, and manganese oxides and, therefore, not bioavailable.

Nickel-containing alloys are used in patients in joint prostheses, sutures, clips, and screws for fractured bones. Corrosion of these implants may lead to elevated nickel levels in the surrounding tissue and to the release of nickel into extracellular fluid (IARC 1990; Ries et al. 2003; Sunderman 1989a; Sunderman et al. 1986, Sunderman et al. 1989c). For example, elevation of nickel blood concentrations (up to 3 times higher than before implantation) has been observed in patients receiving the Amplatzer occluder to repair atrial septal defects up to 1 month following implantation (Ries et al. 2003). However, the nickel concentrations return to preimplantation levels within 12 months. Short-term elevations in nickel concentrations measured in blood and urine of up to a factor of 5 and 10 above preimplant levels, respectively, were seen in patients receiving knee and hip prostheses within 1–2 days of implant (Sunderman et al. 1989c). The rapid rise is attributed to the leaching of nickel from nickel-bearing particles from drills, cutting jigs, and drilling jigs. These nickel concentrations were found to decrease to near preimplant concentrations within 2 weeks of implant. Serum albumin solutions used for intravenous

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infusion fluids have been reported to contain as much as 222 µg nickel/L, but are very rarely encountered. Dialysis fluid has been reported to contain as much as 0.82 µg nickel/L. Studies of nickel in serum pre- and post-dialysis show between 0 and 33% increases in nickel concentrations in patients (IARC 1990).

People who live near or work at facilities in the United States that produce stainless steel and other nickel-containing alloys, oil-fired power plants, coal-fired power plants, refuse incinerators, or waste sites that receive nickel-producing or using industries have the potential to be exposed to levels of nickel in airborne dust, soil, and vegetation that are greater than those for the general population by virtue of their proximity to these sites. Nickel uptake is expected to result from one or more (simultaneous) exposure pathways, such as inhalation, dermal contact, or ingestion of contaminated soil or vegetation. Inhalation and ingestion of particulate matter are likely the main routes of occupational exposures. In the United States, these exposures are minimized through the limiting of allowable concentrations of nickel in air in the workplace (see Chapter 8) and the recommended use of protective clothing and equipment (HSDB 2005). For residents living near NPL sites and other facilities that produce, use, handle, or store nickel or nickel-containing material, many of the nickel concentrations measured in air (0.4912–4,000 ng/m³), surface water (2–20,000 ppb), groundwater (4.2–11,400 ppb), and soils (2–10,522 ppb) offsite from NPL sites (HazDat 2005; Newhook et al. 2003) exceed the average concentrations of nickel in air (6–20 ng/m³), surface water (15–20 ppb), groundwater (3 ppb), and soils (<5,000–700,000 ppb) measured in the United States (ATSDR 2003; Barceloux 1999; Grandjean 1984; NAS 1975; Page 1981; Shacklette and Boerngen 1984). It is likely that the greatest exposures to nickel from these facilities are expected to be through inhalation of particulate matter containing nickel or through ingestion of drinking water obtained from private wells. The relationship between these increased nickel concentrations measured in media offsite of these facilities and exposure of nearby residents to nickel will vary between facilities and depend mainly on the location of a resident to the facility.

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

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

6.8.1 Identification of Data Needs

Physical and Chemical Properties. Except for differences between black and green nickel oxide, the physical and chemical properties of nickel and its compounds reported in Table 4-2 (HSDB 2004) have been adequately characterized.

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

Information on the production, import, export, and use of nickel metal, nickel alloys, and nickel compounds is readily available (ABMS 1994, 2002; Chamberlain 1985; Kirk 1988a, 1988b; Kuck 2002, 2002; NTD 1996; Tien and Howson 1981; USGS 2003). Except for recycling of metal scrap, little information is available regarding the disposal of nickel and its compounds.

Releases according to the TRI database are reported in Tables 6-1 and 6-2 (TRI02 2004). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list. Much of the nickel released to the environment is transferred off-site for disposal and probably landfilled. Nickel wastes from former mining and smelting operations may have been discarded in large tailing piles. Acid conditions are often created in tailing piles from sulfidic ores that increase the potential for leaching (Wood 1987). This is not the case with lateritic deposits such as those found in Riddle, Oregon. Information regarding nickel leaching from slag heaps is important in assessing releases to the environment. More detailed information regarding disposal methods and the form of nickel disposed of is necessary to assess potential nickel exposure.

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Environmental Fate. Nickel is an element and therefore, is not destroyed in the environment. In assessing human exposure, one must consider the form of nickel and its bioavailability. This information is site specific. Data regarding the forms of nickel in air, soil, and sediment are fragmentary and inadequate (Galbreath et al. 2003; Sadiq and Enfield 1984a; Schroeder et al. 1987). Also lacking is adequate information on the transformations that may occur, the transformation rates, and the conditions that facilitate these transformations. Information relating to the adsorption of nickel by soil and sediment is not adequate. In some situations, adsorption appears to be irreversible. In other situations, however, adsorption is reversible. More data would be helpful in detailing those situations where adsorbed nickel may be released and those where release is unlikely.

Bioavailability from Environmental Media. The absorption and distribution of nickel as a result of inhalation, ingestion, and dermal exposure are discussed in Sections 3.4.1 and 3.4.2. Quantitative data relating the physical/chemical properties of nickel (e.g., particle size, chemical forms of nickel) with its bioavailability are available for inhaled nickel. In aqueous media, nickel is in the form of the hexahydrate ion, which is poorly absorbed by most living organisms (Sunderman and Oskarsson 1991), although uptake of nickel into rye and oats has been reported (Smith 1994; Weng et al. 2004). Additional studies that examine the absorption of nickel from soil would be useful.

Food Chain Bioaccumulation. Data are available on the bioconcentration of nickel in fish and aquatic organisms (Birge and Black 1980; EPA 1979; McGeer et al. 2003; Suedel et al. 1994; Zaroogian and Johnson 1984). Higher levels of nickel have been found in gar compared with catfish from the same environment (Winger et al. 1990). More data on different species of fish at different sites would be useful in explaining these results. Data are limited on the nickel levels in wild birds and mammals (Alberici et al. 1989; Dressler et al. 1986; Jenkins 1980). A larger database including information on both herbivorous and carnivorous species living in both polluted and unpolluted environments is desirable in establishing whether nickel biomagnification in the food chain occurs under some circumstances.

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

Representative and recent monitoring data for nickel in air, water, and foods are essential for estimating the extent of exposure from each of these sources. Nickel levels in environmental media are often below

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the detection limit of the analytical method employed. When a substantial fraction of determinations of nickel levels in environmental samples are below the detection limit, an arithmetic mean may not adequately represent the data. Data on the levels of nickel in ambient and indoor air are available (Claiborne et al. 2002; EPA 1986a; Evans et al. 1984; Graney et al. 2004; Kinney et al. 2002; Koutrakis et al. 1992; Kowalczyk et al. 1982; Liou et al. 1987; Galbreath et al. 2003; Saltzman et al. 1985; Sweet et al. 1993; van Winkle and Scheff 2001; Wiersema et al. 1984). Data provided by EPA's National Human Exposure Assessment Study (NHEXAS) have contributed to the assessment of current levels of exposure to nickel by the U.S. population via inhalation, drinking water and food. Analyses of data obtained from the Arizona and EPA Region 5 NHEXAS studies (O'Rourke et al. 1999; Thomas et al. 1999) and another total dietary study (NAS 2002) have provided information on daily dietary nickel intake for these study populations. These data have provided the first update of nickel content within the U.S. diet since the last comprehensive survey of nickel in U.S. drinking water in 1969–1970 (NAS 1975) and the information on dietary nickel that had been limited to one study from North Dakota (Myron et al. 1978). While these recent results are in agreement with ones from Europe (Alberti-Fidanza et al. 2003; IARC 1990), they do differ from the estimated dietary nickel intakes obtained by Moschandreas et al. (2002). Therefore, additional data on nickel content within the U.S. diet, especially information covering a larger geographic area in the United States, is desirable. Also, few data are available regarding nickel levels at contaminated or hazardous waste sites (Agency for Toxic Substances and Disease Registry 2003; Bradley and Morris 1986; Duke 1980b; Taylor and Crowder 1983). This information is necessary for exposure assessment analysis at these sites. This should include monitoring of air and drinking water concentrations of nickel surrounding these sites. Since nickel is found in all soil, studies should focus on waste sites where nickel levels are substantially above those found in ordinary soil.

Exposure Levels in Humans. Nickel levels in body fluids, tissue, hair, nails, and breast milk are available (Andersen and Svenes 2003; DiPietro et al. 1989; Hopfer et al. 1989; IARC 1990; Iyengar 1989; Takagi et al. 1986, 1988). Serum and urine levels in some exposed workers have also been published (Angerer and Lehnert 1990; Barceloux 1999; Bencko et al. 1986; Bernacki et al. 1978; Danadevi et al. 2003; Elias et al. 1989; Ghezzi et al. 1989; Hassler et al. 1983; Morgan and Rouge 1984; Oliveira et al. 2000; Torjussen and Andersen 1979). These data do not refer to populations living around hazardous waste sites that contain elevated levels of nickel. It is recommended that additional studies be conducted that examine biomarkers of exposure or markers of early biological effects, such as changes in gene expression measured by microarrays. These studies could be piloted with *in vitro* cell lines to determine nickel-specific markers, followed by *in vivo* screening of people living near sites that contain levels of nickel that are elevated above background concentrations or who have occupational exposures to nickel.

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

Exposures of Children. This information is necessary for assessing the need to conduct health studies on children. Some data on daily intake of nickel is available for children under the age of 18 years (Thomas et al. 1999), including data for various age ranges of children (Moschandreas et al. 2002; NAS 2002; O'Rourke et al. 1999). The nickel levels in urine are available (Baranowska-Dutkiewicz et al. 1992), but information on levels in other body fluids, tissue, hair, and nails is not available. These data do not refer to populations living around the hazardous waste sites that contain elevated levels of nickel. Additional studies that examine nickel levels in body fluids and tissues from children living near hazardous waste sites that contain elevated levels of nickel would be useful.

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

Exposure Registries. Although there is no U.S. exposure registry for nickel, a Finnish exposure registry for occupational carcinogens exists, and this registry contains information on nickel and inorganic nickel compounds (Grandjean 1984).

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

6.8.2 Ongoing Studies

A number of ongoing studies concerning the fate/transport of nickel and human exposures to nickel were identified in the FEDRIP (2004) database. These studies are summarized in Table 6-6.

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Table 6-6. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Nickel^a

Investigator	Affiliation	Research description	Sponsor
Angle, JS	University of Maryland	Identify indigenous microorganisms that affect both metal solubility in soil and uptake into plants	Hatch
Baligar, VC; Clark, RB; Zelazny, LC; Persaud, N; Ritchey, KD; Martens, DC	Virginia Polytechnical Institute and State University	Evaluate the mineralogy and chemistry of trace elements in soil treated with coal-fired power plant byproducts	USDA
Baker, JC	Virginia Polytechnic Institute	Determine chemical, physical, and soil water status in 1,200 Virginia soil horizons, including quantifying trace metal concentrations	Hatch
Bleam, WF	University of Wisconsin	Characterizing trace metal complexes with humic acids containing thiols or amines	Hatch
Bleam, WF; Helmke, PA	University of Wisconsin at Madison	Improve understanding of how humic substances in soil bind trace metals by elucidating specific binding sites and their affinities for trace metals	USDA
Chaney, RL	Beltsville Agricultural Research Center	Characterize trace element absorbants in municipal, industrial, and agricultural byproduct-amended soils	USDA
Franklin, RE; Mylavarapu, R	Clemson University	Establish baselines for metal concentrations in soils in South Carolina and vicinity; measure metal concentrations in plants grown in soils amended with waste waters and solid wastes	Hatch
Hopkins, DG	North Dakota State University	Evaluate the total and bioavailable trace metals in North Dakota Drift Prairie	Hatch
Koenig, RT	Utah State University	Assess concentrations of metals, phosphorous, and nitrogen in soils amended with biosolids	Hatch
Lave, LB	Carnegie-Mellon University	Development of input-output models for assessing heavy metal flows throughout some 500 economic sectors in the United States	NSF
Martinez, CE	Pennsylvania State University	Characterize the distribution and elemental associations of nickel, copper, and zinc in field-collected soils and evaluate the long-term partitioning and redistribution of these elements using computer modeling	USDA
Odom, JW	Auburn University	Determine the normal occurrence of both total and extractable trace metals in selected Alabama soil profiles	Hatch

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Table 6-6. Ongoing Studies on Environmental Fate and the Potential for Human Exposure to Nickel^a

Investigator	Affiliation	Research description	Sponsor
Parker, DR	University of California	Determine binding constants between mugineic acids and trace metals; evaluate competition between iron and other trace metals in soils in binding reactions with mugineic acids; elucidate mechanisms through which mugineic acids contribute to the uptake of trace metals into plants	USDA
Ross, DS	University of Vermont	Characterize the reactive sites on soil manganese oxides and elucidating the oxidation of trace metals at these sites	Hatch
Sparks, DL	University of Delaware	Determine the effects of reaction conditions and residence time on the sorption/release of important metals/metalloids on soil components and Delaware soils	USDA
Sparks, DL; Ford, RG	University of Delaware	Examine nickel and zinc sorption-desorption kinetic behavior on model and natural soil components, characterize structure of the sorption complex, and investigate effect of competition of soil components with metal-aluminum precipitates	USDA
Sparks, DL; Scheidegger, AM; Lamble, GM	University of Delaware	Determine the effects of residence time on the mechanisms of nickel sorption/release on soils and soils components; develop predictions about long-term fate of nickel in soils	USDA
Thompson, ML; Horton, R; Tabatabai, MA	Iowa State University	Identify and quantify the fundamental processes that determine the fate and transport of metals and pesticides once they are applied to the soil or where they occur in contaminated soils	USDA
Tu, S	Eastern Regional Research Center, Wyndmoor, Pennsylvania	Elucidate the kinetics and mechanisms of heavy metal retention/release by soil mineral colloids as affected by inorganic anions	USDA
Volk, VV; Roseberg, RJ; Baham, J	Oregon State University	Assess potential of plants to remove trace metals from soils and determine impact of trace metals on plant health	USDA

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NSF = National Science Foundation; USDA = U.S. Department of Agriculture

6. POTENTIAL FOR HUMAN EXPOSURE

As part of the Third National Health and Nutrition Evaluation Survey (NHANES III), the Environment Health Laboratory Sciences Division of the National Center for Environment Health, Centers for Disease Control and Prevention, will be analyzing human urine samples for nickel. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population.