## 6. POTENTIAL FOR HUMAN EXPOSURE

## 6.1 OVERVIEW

Vanadium has been identified in at least 319 of the 1,699 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2007). However, the number of sites evaluated for vanadium is not known. The frequency of these sites can be seen in Figure 6-1. All of these sites are located within the United States.

Vanadium is widely distributed in the earth's crust at an average concentration of 100 ppm (approximately 100 mg/kg), similar to that of zinc and nickel (Byerrum 1991). Vanadium is the 22<sup>nd</sup> most abundant element in the earth's crust (Baroch 2006). There are about 65 different vanadium-containing minerals; carnotite, roscoelite, vanadinite, and patronite are important sources of this metal along with bravoite and davidite (Baroch 2006; Lide 2008). It is also found in phosphate rock and certain ores and is present in some crude oils as organic complexes (Lide 2008).

Vanadium is released naturally to the atmosphere by the formation of continental dust, marine aerosols, and volcanic emissions. Vanadium is a constituent of nearly all coal and petroleum crude oils. Eastern U.S. coal has an average vanadium content of approximately 30 ppm, while coal from western states has average content of 15 ppm, and coal from the interior portion of the United States contains an average vanadium concentration of 34 ppm (Byerrum et al. 1974). The average vanadium content of bituminous and anthracite coal is 30 and 125 ppm, respectively (Byerrum et al. 1974). The most important anthropogenic sources of vanadium include the combustion of fossil fuels, particularly residual fuel oils, which constitute the single largest overall release of vanadium to the atmosphere. While the levels of vanadium in residual fuel oil vary by source, levels of 1-1,400 ppm have been reported (Byerrum et al. 1974). Natural gas and distillate fuel oils contain very low or undetectable levels (<0.05 ppm) of vanadium and are not considered a significant source of vanadium to the environment, except in the case of large accidental spills. The natural release of vanadium to water and soils occurs primarily as a result of weathering of rocks and soil erosion. This process usually involves the conversion of the less-soluble trivalent form to the more soluble pentavalent form. Deposition of atmospheric vanadium is also an important source both near and far from industrial plants burning residual fuel oils rich in vanadium. Other anthropogenic sources include leachates from mining tailings, vanadium-enriched slag heaps, municipal sewage sludge, and certain fertilizers. Natural releases to water and soil are far greater overall than anthropogenic releases to the atmosphere.

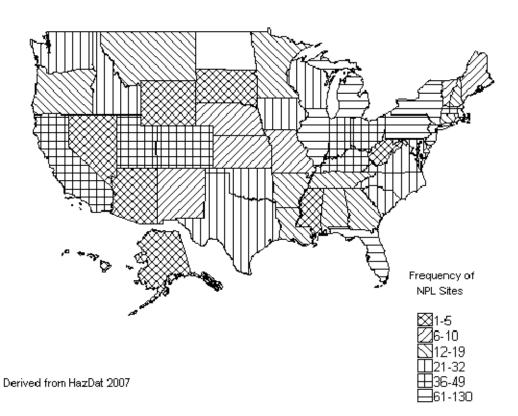


Figure 6-1. Frequency of NPL Sites with Vanadium Contamination

#### 6. POTENTIAL FOR HUMAN EXPOSURE

Ambient atmospheric levels of vanadium are generally low (parts per trillion range) in rural and remote areas and greater in urban locations; however, vanadium levels in both rural and urban locations in the eastern United States tend to be significantly higher than in other areas throughout the country, particularly during winter months. A high density of oil fired power plants that consume vanadium-rich residual fuel oil stretching from southern New York to North Carolina are likely to be the greatest potential source of the high vanadium levels observed in the eastern United States (Polissar et al. 2001). In 2007, the Department of Energy reported that nearly 80% of the residual fuel oil consumed for power generation was purchased in the East Coast districts (DOE 2008).

The general population is exposed to background levels of vanadium primarily through ingestion of food. Vanadium in food is mainly ingested as  $VO^{2+}$  (vanadyl,  $V^{4+}$ ) or  $HVO_4^{2-}$  (vanadate) (Sepe et al. 2003). Vanadium, as elemental vanadium or vanadyl sulfate, is also found in some dietary supplements and multivitamins; consumption of some vanadium-containing supplements may result in intakes of vanadium that would exceed those from food. Workers in industries processing or using vanadium compounds are commonly exposed to higher than background levels of vanadium as vanadium oxides via the inhalation pathway. Exposure to vanadium oxides through inhalation may also be of importance in urban areas, particularly in the northeastern United States where large amounts of residual fuel oil are burned. Other populations possibly exposed to higher-than-background levels, include those ingesting foodstuffs contaminated by vanadium-enriched soil, fertilizers, or sludge. Populations in the vicinity of vanadium-containing hazardous waste sites may also be exposed to higher than background levels. Individuals exposed to cigarette smoke may also be exposed to higher-than-background levels of vanadium.

## 6.2 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005b). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ 10 or more full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities

primarily engaged in solvents recovery services on a contract or fee basis); 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 2005b).

## 6.2.1 Air

Estimated releases of  $5.8 \times 10^4$  pounds (~26 metric tons) of vanadium (except when contained in an alloy) to the atmosphere from 39 domestic manufacturing and processing facilities in 2009, accounted for about 2.8% of the estimated total environmental releases from facilities required to report to the TRI (TRI09 2011). Estimated releases of  $4.8 \times 10^5$  pounds (~218 metric tons) of vanadium compounds to the atmosphere from 510 domestic manufacturing and processing facilities in 2009, accounted for about 1.2% of the estimated total environmental releases from facilities required to report to the TRI (TRI09 2011). These releases are summarized in Tables 6-1 and 6-2.

Natural sources of atmospheric vanadium include continental dust, marine aerosol, and volcanic emissions (Byerrum et al. 1974; Van Zinderen Bakker and Jaworski 1980; Zoller et al. 1973). The quantities entering the atmosphere from each of these sources are uncertain; however, continental dust is believed to account for the largest portion of naturally emitted atmospheric vanadium followed by marine aerosols. Contributions from volcanic emissions are believed to be negligible when compared with the other two sources (Zoller et al. 1973).

Combustion of heavy fuels, especially in oil-fired power plants, refineries, and industrial boilers, and coal are the major source of anthropogenic emissions of vanadium into the atmosphere (Mamane and Pirrone 1998; Sepe et al. 2003). Global anthropogenic atmospheric emission of vanadium as been estimated to be  $2.1 \times 10^5$  metric tons (MT)/year, 3 times higher than vanadium releases due to natural sources. However, other estimates indicated that anthropogenic releases of particulate-bound vanadium (9x10<sup>4</sup> MT/year) were more similar to releases due natural sources, such as continental or volcanic dusts, which have releases of 7x10<sup>4</sup> and 1x10<sup>4</sup> MT/year, respectively) (Mamane and Pirrone 1998).

Fuel oils may contain vanadium in concentrations ranging from 1 to 1,400 ppm, depending on their origin (Byerrum et al. 1974). During the combustion of residual oils organovanadium compounds found in fuel oils are oxidized and transformed into various compounds (e.g., vanadium pentoxide, vanadium tetroxide, vanadium trioxide, and vanadium dioxide). These compounds are emitted as fly ash into the atmosphere (Mamane and Pirrone 1998).

Reported amounts released in pounds per year <sup>b</sup>								per year <sup>b</sup>		
							Total release			
State <sup>c</sup>	$RF^d$	Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site	
AL	1	0	0	0	3,674	0	3,674	0	3,674	
AR	1	2	0	0	0	100	2	100	102	
AZ	2	173	0	0	127,031	0	127,204	0	127,204	
CA	3	467	0	0	418,028	0	418,494	8	418,503	
ID	1	0	0	0	672,592	0	669,256	3,336	672,592	
IL	1	250	0	0	0	1,924	250	1,924	2,174	
KS	3	5,742	0	0	12,279	26,292	17,021	392,292	409,313	
KY	1	8	0	0	0	80	8	80	88	
LA	3	106	4,880	0	49,465	3	4,986	49,468	54,454	
MI	1	7	0	0	4,784	0	4,791	0	4,791	
MS	1	0	0	0	0	0	0	0	0	
ND	1	50,253	11	0	89,062	0	91,196	48,130	139,326	
NH	1	0	0	0	0	0	0	0	0	
ОН	3	516	20	0	51,000	0	536	51,000	51,536	
OR	1	0	0	0	15,458	0	15,458	0	15,458	
PA	1	10	0	0	5	0	15	43,807	43,822	
PR	1	154	0	0	9,911	0	154	9,911	10,065	
SC	1	44	1,934	0	3,046	0	5,024	0	5,024	
TN	2	26	0	0	5,114	417	26	5,531	5,557	
ТΧ	8	544	1,794	0	14,145	0	3,044	13,439	16,483	
VA	1	70	19	0	0	0	89	0	89	
WY	1	218	0	0	118,374	0	118,592	0	118,592	
Total	39	58,590	8,658	0	1,593,968	28,816	1,479,820	619,027	2,098,847	

# Table 6-1. Releases to the Environment from Facilities that Produce, Process, orUse Vanadium (Except When Contained in an Alloy)<sup>a</sup>

<sup>a</sup>The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

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

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

<sup>d</sup>Number of reporting facilities.

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

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>9</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.

<sup>i</sup>Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown

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

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI09 2011 (Data are from 2009)

		Reported amounts released in pounds per year <sup>b</sup>								
							Total release			
State <sup>c</sup>	RF <sup>d</sup>	Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off- site	
AL	19	4,721	18,841	0	1,111,800	21,000	1,134,113	22,250	1,156,363	
AK	1	0	6	0	33,000	0	33,006	0	33,006	
AR	9	12,419	151,601	0	1,195,161	1,450	1,358,806	1,824	1,360,630	
AZ	7	1,237	5	0	250,677	0	251,913	5	251,918	
CA	14	723	1,605	0	27,232	90	1,661	27,990	29,650	
CO	10	1,290	107	0	268,477	225	178,174	91,924	270,098	
СТ	2	0	0	0	31,700	0	0	31,700	31,700	
DE	4	753	11,193	0	344,027	20,358	56,479	319,852	376,331	
FL	21	19,222	2,473	26,719	1,700,859	235,222	695,760	1,288,735	1,984,494	
GA	17	18,478	10,508	0	1,233,511	14,610	1,213,179	63,928	1,277,107	
HI	1	45	0	0	30,353	0	45	30,353	30,398	
IA	7	1,496	595	0	287,488	16,334	216,579	89,334	305,913	
ID	1	896	1,100	0	2,263,589	11	2,265,585	11	2,265,596	
IL	19	7,940	10,342	0	424,580	114,035	320,274	236,623	556,897	
IN	28	11,060	10,644	0	2,471,511	2,158	2,187,747	307,626	2,495,372	
KS	8	9,033	0	0	280,360	0	289,125	268	289,393	
KY	18	58,135	23,180	0	4,050,595	18,790	4,131,218	19,482	4,150,700	
LA	25	149,968	43,257	23	361,536	39,140	515,936	77,988	593,924	
MA	3	725	1,136	0	18,903	0	4,192	16,572	20,764	
MD	10	3,372	1,455	0	101,105	263,964	70,700	299,196	369,896	
ME	2	882	4,549	0	3,654	0	9,085	0	9,085	
MI	18	3,189	7,537	0	727,433	1,695	608,128	131,726	739,854	
MN	4	1,773	45	0	277,611	128				
МО	12	5,251	28	0	356,710	0				
MS	9	924	129,473	1,321,526	2,640,672	36,000				
MT	4	3,236	190	0	187,827	7,630				
NC	17	3,686	9,149	0	1,372,162	1,979				
ND	3	1,114	1	0	143,187	681	139,519			
NE	4	3,001	0	0	192,186	0				
NH	1	94	0	0	15,950	0	2,594			
NJ	7	1,241	5,300	0	7,483		6,541			
NM	4	1,432	165	0	560,034	0				
NV	4	20	0	0	1,994,350	0				
NY	7	15,567	1,137	0	113,671	112,819				
OH	25	55,568	1,638	2,757	2,016,980	249,860			2,326,802	
OK	11	25,855	1,000	2,707	113,108	0				

# Table 6-2. Releases to the Environment from Facilities that Produce, Process, orUse Vanadium Compounds<sup>a</sup>

	Reported amounts released in pounds per year <sup>b</sup>								
							Total release		
State <sup>c</sup>	$RF^{d}$	Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off- site
OR	1	255	0	0	2,200	0	2,455	0	2,455
PA	32	19,104	2,077	0	1,659,005	2,107	995,706	686,587	1,682,294
SC	13	5,675	9,532	0	339,405	46,078	336,669	64,021	400,690
SD	1	114	0	0	23,452	0	21,126	2,440	23,566
TN	12	2,025	24,887	0	1,896,639	145	1,837,999	85,697	1,923,696
ТΧ	42	11,942	67,356	18,329	1,910,956	633	1,874,004	135,212	2,009,216
UT	8	808	1,000	0	282,299	394	282,147	2,354	284,501
VA	1	1,933	8,380	0	539,812	3,323	486,961	66,487	553,448
VI	13	1,550	4,965	0	12,771	352	11,953	7,685	19,638
WA	2	462	126	0	52,693	0	52,963	318	53,281
WI	12	4,165	1,140	0	274,365	87,446	38,993	328,123	367,116
WV	13	3,516	976	0	1,577,671	4,900	1,149,666	437,397	1,587,063
WY	4	1,855	0	0	290,674	0	219,629	72,900	292,529
Total	510	477,749	567,708	1,369,354	36,071,424	1,308,263	33,193,236	6,601,262	39,794,498

# Table 6-2. Releases to the Environment from Facilities that Produce, Process, orUse Vanadium Compounds<sup>a</sup>

<sup>a</sup>The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

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

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

<sup>d</sup>Number of reporting facilities.

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

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>g</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.

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

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

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI09 2011 (Data are from 2009)

Vanadium has not been identified in air collected at current or former NPL hazardous waste sites where vanadium was detected in some environmental media (HazDat 2007).

## 6.2.2 Water

Estimated releases of 8,658 pounds (~4 metric tons) of vanadium (except when contained in an alloy) to surface water from 39 domestic manufacturing and processing facilities in 2009, accounted for about 0.4% of the estimated total environmental releases from facilities required to report to the TRI (TRI09 2011). Estimated releases of  $5.7 \times 10^5$  pounds (~258 metric tons) of vanadium compounds to surface water from 510 domestic manufacturing and processing facilities in 2009, accounted for about 1.4% of the estimated total environmental releases from facilities required to report to the TRI (TRI09 2011). These releases are summarized in Tables 6-1 and 6-2.

Natural sources of vanadium release to water include wet and dry deposition, soil erosion, and leaching from rocks and soils. The largest amount of vanadium release occurs naturally through water erosion of land surfaces. It has been estimated that approximately 32,300 tons of vanadium are dissolved and transported to the oceans by water, and an additional 308,650 tons are thought to be transported in the form of particulate and suspended sediment (Van Zinderen Bakker and Jaworski 1980).

Anthropogenic releases to water and sediments are far smaller than natural sources (Van Zinderen Bakker and Jaworski 1980). Such sources of vanadium in water may include leaching from the residue of ores and clays, vanadium-enriched slags, urban sewage sludge, and certain fertilizers, all of which are subjected to rain and groundwater drainage, as well as leachate from ash ponds and coal preparation wastes (Byerrum et al. 1974; Van Zinderen Bakker and Jaworski 1980). Leaching may potentially occur from landfills and from the airborne particulate matter that is deposited in areas with high residual fuel oil combustion, although neither of these release sources is documented.

Vanadium has been identified in groundwater and surface water at 224 and 129 sites, respectively, of the 319 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2007).

## 6.2.3 Soil

Estimated releases of  $1.6 \times 10^6$  pounds (~725 metric tons) of vanadium (except when contained in an alloy) to soils from 39 domestic manufacturing and processing facilities in 2009, accounted for about 75%

#### 6. POTENTIAL FOR HUMAN EXPOSURE

of the estimated total environmental releases from facilities required to report to the TRI (TRI09 2011). Estimated releases of  $3.6 \times 10^7$  pounds (~ $1.6 \times 10^4$  metric tons) of vanadium compounds to soils from 510 domestic manufacturing and processing facilities in 2009, accounted for about 91% of the estimated total environmental releases from facilities required to report to the TRI (TRI09 2011). These releases are summarized in Tables 6-1 and 6-2.

Natural releases of vanadium to soil result from weathering of rock-bearing vanadium minerals, precipitation of vanadium particulate from the atmosphere, deposition of suspended particulate from water, and plant and animal wastes. The largest amount of vanadium released to soil occurs through the natural weathering of geological formations (Byerrum et al. 1974; Van Zinderen Bakker and Jaworski 1980).

Anthropogenic releases of vanadium to soil are less widespread than natural releases and occur on a smaller scale. These include the use of certain fertilizers containing materials with a high vanadium content such as rock phosphate (10–1,000 mg/kg vanadium), superphosphate (50–2,000 mg/kg vanadium), and basic slag (1,000–5,000 mg/kg vanadium) (Van Zinderen Bakker and Jaworski 1980) as well as disposal of industrial wastes such as slag heaps and mine tailings. Additional release to the environment may also result from the disposal of vanadium-containing wastes in landfills, although this has not been specifically documented, and from wet and dry deposition of airborne particulate, particularly in areas with high levels of residual fuel oil combustion (Byerrum et al. 1974).

Vanadium has been identified in soil at 172 sites and in sediment at 44 sites collected from 319 NPL hazardous waste sites, where vanadium was detected in some environmental media (HazDat 2007).

## 6.3 ENVIRONMENTAL FATE

## 6.3.1 Transport and Partitioning

The global biogeochemical cycling of vanadium is characterized by releases to the atmosphere, water, and land by natural and anthropogenic sources, long-range transportation of particles in both air and water, wet and dry deposition, adsorption, and complexing. Vanadium generally enters the atmosphere as an aerosol. From natural sources, vanadium is probably in the form of mineral particles; it has been suggested that these may frequently be in the less-soluble trivalent form (Byerrum et al. 1974; Zoller et al. 1973). From human-made sources, almost all of the vanadium released to the atmosphere is in the form of simple or complex vanadium oxides (Byerrum et al. 1974).

The size distribution of vanadium-bearing particles in the atmosphere is substantially altered during longrange transportation (Zoller et al. 1973). Natural sources of vanadium, as well as man-made sources such as ore-processing dust, tend to release large particles that are more likely to settle near the source. Smaller particles, such as those emitted from oil-fueled power plants, have a longer residence time in the atmosphere and are more likely to be transported farther away from the site of release (Zoller et al. 1973). Vanadium transported within the atmosphere is eventually transferred to soil and water on the earth's surface by wet and dry deposition and dissolution in sea water (Duce and Hoffman 1976; Van Zinderen Bakker and Jaworski 1980). Eventually, in the course of biogeochemical movement between soil and water, these particulates are adsorbed to hydroxides or associated with organic compounds and are deposited on the sea bed (WHO 1988).

Deposition rates ranging from 20.5 to 84.9  $\mu$ g/cm<sup>2</sup>/day of vanadium were reported in urban dust collected between March and September 2002 from six locations Adapazarí, Turkey (Dundar 2006). Vanadium is considered a marker of air pollution emitted from residual oil and coal combustion (Mamane and Pirrone 1998).

The transport and partitioning of vanadium in water and soil is influenced by pH, redox potential, and the presence of particulate. In fresh water, vanadium generally exists in solution as the vanadyl ion ( $V^{4+}$ ) under reducing conditions and the vanadate ion ( $V^{5+}$ ) under oxidizing conditions, or as an integral part of, or adsorbed onto, particulate matter (Wehrli and Stumm 1989). The chemical formulas of the vanadyl species most commonly reported in fresh water are  $VO^{2+}$  and  $VO(OH)^+$ , and the vanadate species are  $H_2VO_4^-$  and  $HVO_4^{2-}$  (Wehrli and Stumm 1989). The partitioning of vanadium between water and sediment is strongly influenced by the presence of particulate in the water. Both vanadate and vanadyl species are known to bind strongly to mineral or biogenic surfaces by adsorption or complexing (Wehrli and Stumm 1989). Thus, vanadium is transported in water in one of two ways: solution or suspension. It has been estimated that only 13% is transported in solution, while the remaining 87% is in suspension (WHO 1988).

Upon entering the ocean, vanadium in suspension or adsorbed and/or absorbed onto particulate is deposited upon the sea bed (WHO 1988). The fate of the remaining dissolved vanadium is more complex. Only about 0.001% of vanadium entering the oceans is estimated to persist in soluble form (Byerrum et al. 1974). Adsorption/absorption and biochemical processes are thought to contribute to the extraction of vanadium from sea water (WHO 1988). Adsorption to organic matter as well as to

#### 6. POTENTIAL FOR HUMAN EXPOSURE

manganese oxide and ferric hydroxide, demonstrated by the high particle-water partition coefficient of  $5.7 \times 10^5$  L/kg for the adsorption of manganese oxide in sea water, results in the precipitation of the dissolved vanadium (Wehrli and Stumm 1989; WHO 1988). Biochemical processes are also of importance in the partitioning from sea water to sediment (WHO 1988). Some marine organisms, in particular the ascidians (sea squirts), bioconcentrate vanadium very efficiently, attaining body concentrations approximately 10,000 times greater than the ambient sea water (Byerrum et al. 1974). Upon the death of the organism, the body burden adds to the accumulation of vanadium in silt (WHO 1988). The extent to which either bioconcentration or adsorption dominates is uncertain (WHO 1988).

In general, marine plants and invertebrates contain higher levels of vanadium than terrestrial plants and animals. In the terrestrial environment, bioconcentration is more commonly observed amongst the lower plant phyla than in the higher, seed-producing phyla. The vanadium levels in terrestrial plants are dependent upon the amount of water-soluble vanadium available in the soil, pH, and growing conditions. It has been found that the uptake of vanadium into the above-ground parts of many plants is low, although root concentrations have shown some correlation with levels in the soil (Byerrum et al. 1974). Certain legumes, such as Astralagus preussi, have been shown to be vanadium accumulators. Vanadium is believed to replace molybdenum as a specific catalyst in nitrogen fixation (Cannon 1963), and the root nodules of these plants may contain vanadium levels three times greater than those of the surrounding soil (Byerrum et al. 1974). Of the few plants known to actively accumulate vanadium, Amanita muscaria, a poisonous mushroom, has been demonstrated to contain levels up to 112 ppm (dry weight). Vanadium appears to be present in all terrestrial animals, but, in vertebrates, tissue concentrations are often so low that detection is difficult. The highest levels of vanadium in terrestrial mammals are generally found in the liver and skeletal tissues (Van Zinderen Bakker and Jaworski 1980; WHO 1988). No data are available regarding biomagnification of vanadium within the food chain, but human studies suggest that it is unlikely; most of the 1–2% vanadium that appears to be absorbed by humans following ingestion is rapidly excreted in the urine with no evidence of long-term accumulation (Fox 1987).

The form of vanadium present in the soil is determined largely by the parent rock. Ferric hydroxides and solid bitumens (organic) constitute the main carriers of vanadium in the sedimentation process. Iron acts as a carrier for trivalent vanadium due to the high affinity between trivalent vanadium and trivalent iron, and is responsible for its diffusion through molten rocks where it becomes trapped during crystallization. The mobility of vanadium in soils is affected by the pH of the soil. Relative to other metals, vanadium is fairly mobile in neutral or alkaline soils, but its mobility decreases in acidic soils (Van Zinderen Bakker and Jaworski 1980). Similarly, under oxidizing, unsaturated conditions, some mobility is observed, but

#### 6. POTENTIAL FOR HUMAN EXPOSURE

under reducing, saturated conditions, vanadium is immobile (Van Zinderen Bakker and Jaworski 1980). In a 30-month field study to examine the movement of metal ions through a profile of an acidic loamy sand soil from the Upper Coastal Plain (South Carolina), <3% of the applied vanadium, as dissolved salt (vanadyl sulfate), was found to move below the surface 7.5 cm region (Martin and Kaplan 1998). Buchter et al. (1989) reported log  $K_d$  values for various metal ions in 11 soils from 7 states in the U.S. (Louisiana, South Carolina, Hawaii, Iowa, New Hampshire, New Mexico, and Florida). Log  $K_d$  values for vanadium (applied as ammonium vanadate) ranged from 1.035 in Calciorthid soil from New Mexico (pH 8.5, 0.44% total organic carbon [TOC], 70.0% sand, 19.3% silt, 10.7% clay) to 3.347 in Kula soil from Hawaii (pH 5.9, 6.62% TOC, 73.7% sand, 25.4% silt, 0.9% clay).

## 6.3.2 Transformation and Degradation

As an element, vanadium cannot be degraded in the environment, but may undergo various precipitation or ligand exchange reactions. Vanadium in compounds may undergo oxidation-reduction reactions under various environmental conditions. Vanadium can be complexed by various ligands present in the environment (e.g., fulvic and humic acids). Despite forming complexes with organic matter, it is generally not incorporated into organic compounds. Thus, transformation occurs primarily between various inorganic compounds during its movement through the environment, and biotransformation is not considered to be an important environmental fate process. Vanadium can exist in many different oxidation states, ranging from -2 to +5; however, under environmental conditions, vanadium can exist in the +3, +4, or +5 oxidation states, with the +5 oxidation state being the most prevalent under most environmental conditions (Crans et al. 1998).

### 6.3.2.1 Air

Vanadium-containing particulates emitted to the atmosphere from anthropogenic sources are frequently simple or complex oxides (Byerrum et al. 1974) or may be associated with sulfates (Zoller et al. 1973). Generally, lower oxides formed during combustion of coal and residual fuel oils, such as vanadium trioxide, undergo further oxidation to the pentoxide form, often before leaving the stacks (EPA 1985a). The average residence time for vanadium in the atmosphere is unknown as the particle size varies considerably. An estimated residence time of about 1 day has been proposed for the settling of fly ash vanadium pentoxide when associated with hydrogen sulfate (EPA 1985a).

## 6.3.2.2 Water

Vanadium entering water by leaching from vanadium-containing rocks is rapidly oxidized from lesssoluble vanadium(III) to more-soluble vanadium(V), which is the most common oxidation state of vanadium found in surface waters (Byerrum et al. 1974; Crans et al. 1998). In water, vanadium can undergo hydrolytic reactions, forming oligomeric anionic species. The equilibrium of vanadium(V) in solution is sensitive to vanadium concentration, pH, ionic strength, and oxidation-reduction potential (Crans et al. 1998). The species of vanadium most likely to be found in sea water are  $(H_2V_4O_{13})^{4-}$ ,  $HVO_4^{2-}$ , and  $VO^{3-}$  (Van Zinderen Bakker and Jaworski 1980). Vanadium(III) is only found in very reducing environments or is complexed to organic ligands (Crans et al. 1998). Vanadium is continuously precipitated from sea water by ferric hydroxides and organic matter (WHO 1988) and forms sediments on the seabed.

## 6.3.2.3 Sediment and Soil

There are about 65 different vanadium-containing minerals (Baroch 2006; Lide 2008). The main vanadium-containing minerals include carnotite, cuprodescloizite, descloizite, mottramite, patronite, roscoelite, and vanadinite (Crans et al. 1998). Vanadium exists in its +3 to +5 oxidation states in these minerals. Vanadium(V) is more soluble and is easily leached from soils into water. The vanadium oxides, carnotite, cuprodescloizite, descloizite, mottramite, and vanadinite, are mostly vanadium(V) minerals and comprise most of the vanadium-containing minerals. Roscoelite contains vanadium(III), and the exact chemical composition of patronite is not known (Crans et al. 1998). Weathering of rocks and minerals during soil formation may extract vanadium in the form of a complex anion that may remain in the soil or enter the hydrosphere. Vanadium remains in the soil after being precipitated from the weathering solution. This can be brought about by precipitation with polyvalent cations such as divalent calcium and divalent copper, by binding with organic complexing agents, adsorbing onto anion exchangers such as clay particles in the soil, and coprecipitating and adsorbing to hydrous ferric oxide in the soil (Van Zinderen Bakker and Jaworski 1980). In the presence of humic acids, mobile metavanadate anions can be converted to the immobile vanadyl cations resulting in local accumulation of vanadium (Van Zinderen Bakker and Jaworski 1980).

## 6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to vanadium depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of

#### 6. POTENTIAL FOR HUMAN EXPOSURE

vanadium 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 vanadium 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 vanadium in a variety of environmental media are detailed in Chapter 7.

## 6.4.1 Air

Levels of vanadium measured in ambient air vary widely between rural and urban locations, time of season, and geographical location. In general, urban locations often tend to have greater atmospheric levels of vanadium as compared to rural sites since there is a larger density of combustion sources capable of emitting particulate matter containing vanadium to the environment. Sweet et al. (1993) reported average vanadium concentrations of 3.0 and 3.0  $ng/m^3$  (fine particles, <2.5 µm) and 3.7 and 3.0  $ng/m^3$ (coarse particles, 2.5–10 µm) in samples of inhalable particulate matter collected over a 3-year sampling period in southeast Chicago and East St. Louis Illinois, respectively. The average vanadium concentrations in fine particulate matter ( $<2.5 \,\mu$ m) measured as part of the Harvard Six Cities Studies between 1979 and 1988 were 23.2, 2.0, 1.4, 0.1, 10.5, and 0.6 ng/m<sup>3</sup> in Watertown, Massachusetts; St. Louis, Missouri; Kingston-Harriman, Tennessee; Portage, Wisconsin; Steubenville, Ohio; and Topeka, Kansas, respectively (Laden et al. 2000). Average vanadium concentrations in fine and coarse particulate matter collected from a rural site in Bondville, Illinois were 0.8 and  $1.2 \text{ ng/m}^3$ , respectively (Sweet et al. 1993). Aerosol sampling ( $PM_{2.5}$  fraction) was conducted from 1988 to 1995 at a rural location in Underhill, Vermont (Polissar et al. 2001). A geometric mean concentration of 0.82 ng/m<sup>3</sup> was reported for vanadium, with seasonal maxima occurring during the winter and spring months and minimum concentrations observed during the summer months. A factor analysis method applied to the data determined that the most likely sources of the vanadium were oil fired power plants predominantly located in eastern Virginia, Pennsylvania, southern New York, New Jersey, Maryland, and Delaware (Polissar et al. 2001). Measurements obtained at five different rural sites in northwestern Canada were found have average vanadium concentrations of  $0.72 \text{ ng/m}^3$  (range  $0.21-1.9 \text{ ng/m}^3$ ) (Zoller et al. 1973). Between the years 1965 and 1969, average ambient vanadium concentrations in rural air in the United States ranged from <1 to 40 ng/m<sup>3</sup> (Byerrum et al. 1974), although some rural areas may have levels as high as 64  $ng/m^3$  due to localized burning of fuel oils with a high vanadium content (WHO 1988). Vanadium concentrations in air samples collected from a rural forest in Denmark that received heavy deposition from European cities were 11.5 and 4.4 ng/m<sup>3</sup> in samples from 1979 to 1980 and 2002 to 2005, respectively (Hovmand et al. 2008).

#### 6. POTENTIAL FOR HUMAN EXPOSURE

Northeastern locations in the United States typically have higher atmospheric levels of vanadium as compared to other regions of the country. U.S. cities were divided into two groups based on the levels of vanadium present in the atmosphere and geographic location (Zoller et al. 1973). The first group of cities is widely distributed throughout the United States and is characterized by ambient air vanadium concentrations that range from 3 to 22 ng/m<sup>3</sup>, with an average concentration of 11 ng/m<sup>3</sup> (approximately 20 times that of remote areas). Cities in the second group, primarily located in the northeastern United States, had vanadium concentrations in air that ranged from 150 to 1,400 ng/m<sup>3</sup> with an average of 620 ng/m<sup>3</sup> (Zoller et al. 1973). The variation is attributed to the use of large quantities of residual fuel oil for the generation of heat and electricity, particularly during winter months

Atmospheric levels of vanadium at remote sites tend to be lower since both natural and anthropogenic emissions are typically negligible. Vanadium concentrations measured over the South Pole ranged from 0.001 to 0.002 ng/m<sup>3</sup> (WHO 1988) and are frequently 2 orders of magnitude smaller than those over the ocean at middle latitudes (WHO 1988). For example, vanadium concentrations in air measurements taken at nine rural sites located in the Eastern Pacific averaged 0.1 ng/m<sup>3</sup> (range 0.02–0.8 ng/m<sup>3</sup>). Atmospheric aerosols were collected from Mt. Everest in May–June, 2005; vanadium concentrations ranged from 0.9 to 3.8 ng/m<sup>3</sup>, with a mean of 1.4 ng/m<sup>3</sup> (Cong et al. 2008). Vanadium concentrations at other remote locations of 0.044 and 0.0039 ng/m<sup>3</sup> were reported for Greenland, 1988–1989 and Terra Nova Bay, Antarctica, 2000–2001, respectively (Cong et al. 2008; Mosher et al. 1993).

Vanadium was detected in exhaust aerosol collected from the Elbtunnel, a major highway tunnel in Hamburg, Germany, at an average concentration of 14.8 ng/m<sup>3</sup> (range: 7.6–36.9 ng/m<sup>3</sup>) (Dannecker et al. 1990). Fine atmospheric particulate  $PM_{2.5}$  (particles with diameters of <2.5 µm) were collected from November 2000 to September 2001 in Guaynabo, Puerto Rico, an urban industrialized area, and in Fajardo, Puerto Rico, a less polluted reference site (Figueroa et al. 2006). Vanadium concentrations in the  $PM_{2.5}$  were 40 and 1.4 ng/m<sup>3</sup> for Guaynabo and Fajardo, respectively. Mean urban vanadium concentrations in winter and summer air (fine and course particulate combined) collected from the Birmingham University campus, Edgbaston, United Kingdom in January-February 1992 and July-August 1992 were 11.2 and 3.5 ng/m<sup>3</sup>, respectively. Vanadium concentrations were higher in the fine particle fraction, 7.6 and 2.3 ng/m<sup>3</sup> (winter and summer), as compared to the coarse particle samples, 3.6 and 1.2 ng/m<sup>3</sup> (winter and summer) (Harrison et al. 1996). Mean vanadium concentrations in air samples from a central Copenhagen street (January–March 1992 and February–March 1993) and a city park (January–March 1992) were reported to be 12 and 10 ng/m<sup>3</sup>, respectively (Nielsen 1996). Smith et al.

#### 6. POTENTIAL FOR HUMAN EXPOSURE

(1996) reported mean vanadium concentrations in air samples collected from a city site, a rural site, and an industrial site in Lahore, Pakistan in 1992–1993 of 127, 161, and 253 ng/m<sup>3</sup>, respectively. Mean vanadium concentrations in air samples of 10, 180, and 110 ng/m<sup>3</sup> were reported in Karachi, Pakistan; Calcutta, India; and Bombay, India, respectively (Smith et al. 1996). Schroeder et al. (1987) reported concentration ranges of vanadium associated with particulate matter in the atmosphere: 0.001–14 ng/m<sup>3</sup> (remote areas); 2.7–97 ng/m<sup>3</sup> (rural); 10–130 ng/m<sup>3</sup> (urban Canada); 0.4–1,460 ng/m<sup>3</sup> (urban United States); 11–73 ng/m<sup>3</sup> (urban Europe); and 1.7–180 ng/m<sup>3</sup> (urban other).

Vanadium and nickel were measured in air particulate samples collected during and after the Kuwait oil fires (from March 1991 to July 1992) at Dhahran, Saudi Arabia (Sadiq and Mian 1994). Vanadium concentrations ranged from not detected to 1,165.8 ng/m<sup>3</sup> in the inhalable ( $PM_{10}$ , <10 µm) and from not detected to 160.26 ng/m<sup>3</sup> in the total suspended particulate. The minimum vanadium concentration was found in samples collected in December 1991 and gradually increased through May 1992.

Air sampling in homes in two New York counties in the winter of 1986 measured various contaminants in the indoor air (Koutrakis et al. 1992). Mean vanadium concentrations in indoor air of non-source homes (no kerosene heaters, wood stoves, or cigarette smokers), wood-burning homes, kerosene heater homes, and smoking homes were 5, 4, 6, and 6 ng/m<sup>3</sup>, respectively. Miguel et al. (1995) reported vanadium concentrations in samples of indoor air from non-industrial office workplaces and restaurants in the cities of Sao Paulo and Rio de Janeiro, Brazil in the summer of 1993 ranging from less than the detection limit to 0.360  $\mu$ g/m<sup>3</sup>. Kinney et al. (2002) reported mean winter and summer vanadium concentrations of 9.49 and 4.17 ng/m<sup>3</sup> in indoor air (particle-associated) in 38 homes sampled in 1999 in the West Central Harlem section of New York City. A mean vanadium concentration of 0.8 ng/m<sup>3</sup> was reported inside patrol cars of ten nonsmoking North Carolina State Highway Patrol troopers during 25 work days (3 pm to midnight shift) during August–October of 2001 (Riediker et al. 2003).

## 6.4.2 Water

Levels of vanadium in fresh water illustrate geographic variations produced by differences in effluents and leachates, from both anthropogenic and natural sources, entering the water table. Vanadium concentrations in water can range from approximately 0.2 to >100  $\mu$ g/L depending on geographical location (Sepe et al. 2003). Vanadium was detected in 3,387 of 3,625 surface water samples recorded in the STORET database for 2007–2008 at concentrations ranging from 0.04 to 104  $\mu$ g/L in samples where vanadium was detected (EPA 2009). Measurements of vanadium in such natural fresh waters as the

#### 6. POTENTIAL FOR HUMAN EXPOSURE

Animas, Colorado, Green, Sacramento, San Joaquin, and San Juan Rivers, as well as some fresh water supplies in Wyoming, range from 0.3 to 200  $\mu$ g/L (Byerrum et al. 1974; Van Zinderen Bakker and Jaworski 1980). The presence of naturally occurring uranium ores resulted in rivers in the Colorado Plateau containing vanadium concentrations of up to 70  $\mu$ g/L, and in Wyoming, vanadium concentrations in water were found to range from 30 to 220  $\mu$ g/L (Byerrum et al. 1974).

Taylor et al. (2001) reported vanadium concentrations of <0.05  $\mu$ g/L in water collected in June and September 1994 from the Alamosa River, Colorado and 6.2  $\mu$ g/L in water collected in September 1992 from Big Arsenic Spring, New Mexico. Saleh and Wilson (1999) reported various metal concentrations in surface water from the Houston Ship Channel, Texas; vanadium concentrations ranged from 4.062 to 115.600  $\mu$ g/L in samples from Buffalo Bayou and the Washburn Tunnel, respectively. Coal mining activity in the west-central region of Indiana has resulted in a number of sites where surface waters are contaminated with acidic mine drainage. Surface water samples collected from 12 locations in westcentral Indiana that have been contaminated with acidic mine drainage were reported to contain vanadium at concentrations ranging from 0.17 to 0.66 mg/L (Allen et al. 1996). Kennish (1998) reported vanadium concentrations ranging from 1.0 to 38 nmol/L (0.05–1.9  $\mu$ g/L) in waters from U.S. estuaries and 32 nmol/L (1.6  $\mu$ g/L) in U.S. coastal marine waters.

Levels in sea water are considerably lower than those in fresh water because much of the vanadium is precipitated (Byerrum et al. 1974; Van Zinderen Bakker and Jaworski 1980). Vanadium concentrations measured usually average 1–3  $\mu$ g/L (Sepe et al. 2003; Van Zinderen Bakker and Jaworski 1980), although levels as high as 29  $\mu$ g/L have been reported (Byerrum et al. 1974). The total content of vanadium in sea water has been estimated to be  $7.5 \times 10^{12}$  kg ( $7.5 \times 10^{9}$  metric tons) (Byerrum et al. 1974). Mean vanadium concentrations ranging from 2.08 to 2.60  $\mu$ g/L were reported in seawater samples collected along the Saudi coast of the Arabian Gulf (Sadiq et al. 1992b).

Fiorentino et al. (2007) measured vanadium concentrations in groundwater collected from the southwest of the Province of Buenos Aires, Argentina; all samples contained vanadium, and concentrations ranged from 0.05 to 2.47 mg/L. Groundwater samples collected from 104 monitoring wells from shallow aquifers beneath an industrial city in the Eastern Province of Saudi Arabia contained vanadium concentrations that ranged from 0.04 to 55.69  $\mu$ g/L, with a mean concentration of 7.46  $\mu$ g/L (Sadiq and Alam 1997).

#### 6. POTENTIAL FOR HUMAN EXPOSURE

Vanadium is on the EPA Drinking Water Contaminant Candidate List (CCL). The contaminants on this list are known or anticipated to occur in public water systems; however, they are currently not regulated by existing national primary drinking water regulation. Research is ongoing to determine whether regulations are needed (EPA 2008).

Mean vanadium concentrations in tap water collected from homes participating in a dietary study in EPA Region V (Indiana, Illinois, Michigan, Minnesota, Ohio, and Wisconsin) for the National Human Exposure Assessment Survey (NHEXAS) were 1.2 and 1.0  $\mu$ g/L, respectively, in samples collected after running the water at high velocity for 3 minutes (flushed tap water) and after there had been no usage of any tap water or toilet in the home for the previous 4 hours (standing tap water) (Thomas et al. 1999).

As part of the National Water-Quality Assessment Program of the U.S. Geological Survey (USGS), water samples were collected during 1991–2004 from domestic wells (private wells used for household drinking water) for analysis of drinking-water contaminants. Vanadium was detected in 452 of 662 samples, with a median concentration of 1.29  $\mu$ g/L (USGS 2009a).

Lagerkvist et al. (1986) summarized older reports from the 1960s and 1970s regarding vanadium concentrations in drinking water. One report stated that 91% of drinking water samples analyzed from U.S. sources had vanadium concentrations below 10  $\mu$ g/L, with an average concentration of 4.3  $\mu$ g/L. In another report, the typical vanadium concentrations in drinking water were about 1  $\mu$ g/L.

## 6.4.3 Sediment and Soil

Vanadium is widely distributed in the earth's crust at an average concentration of 100 ppm (approximately 100 mg/kg) (Byerrum 1991). The level of vanadium measured in soil is closely related to the parent rock type (Van Zinderen Bakker and Jaworski 1980; Waters 1977). A range of 3–310 mg/kg has been observed, with tundra podsols and clays exhibiting the highest concentration, 100 and 300 mg/kg, respectively (Byerrum et al. 1974). The average vanadium content of soils in the United States is 200 mg/kg (Byerrum et al. 1974) and seems to be most abundant in the western United States, especially the Colorado Plateau (Cannon 1963; Grayson 1983).

Gallagher et al. (2008) measured various metal concentrations in soils collected during the summer of 2005 from a site in Jersey City, New Jersey on the west bank of Upper New York Bay. This land was originally an intertidal mud flat and a salt marsh that was filled during 1860–1919 with material

#### 6. POTENTIAL FOR HUMAN EXPOSURE

consisting of mostly debris from construction projects and refuse from New York City. It was used as a railroad yard until 1967. The site was then transferred to the New Jersey Division of Parks and Forestry in 1970. Vanadium concentrations in soil collected from this site ranged from below the detection limit ( $<0.01 \mu g/g$ ) to  $317 \mu g/g$ , with a median value of 56.4  $\mu g/g$  (Gallagher et al. 2008). Metal concentrations were measured in two alluvial soils from the lower Mississippi River Delta. Median vanadium concentrations of 3.2 and 3.8  $\mu g/g$  were reported in freshly deposited alluvium soil from Bonnet Carré Spillway and in urban soil samples from New Orleans, respectively (Mielke at el. 2000).

Various trace elements were measured in 13 surface soils collected from southwestern Saskatchewan, Canada (Mermut et al. 1996). Fertilizers and pesticides are the two major anthropogenic sources of trace elements in the Canadian Prairies. Vanadium concentrations ranged from 31.75 mg/kg in Hatton soil (0– 13 cm, pH 6.2, 1.32% organic content [OC], 6% clay) to 180.06 mg/kg in Sceptre soil (90–105 cm, pH 8.0, 0.85% OC, 73% clay). Clay soils were found to contain more vanadium that other soils (Mermut et al. 1996). Vanadium concentrations in 16 soil samples collected in May 2000 in the vicinity of a cement plant in Catalonia, Spain ranged from 5.6 to 12.4 mg/kg dry weight. These values were generally lower than vanadium levels found in urban areas (Schuhmacher et al. 2002). The geometric mean vanadium concentrations in 112 samples street dust and 40 samples of urban soil collected in Aviles, Northern Spain were 28.1 (range 25.0–34.0) and 34.1 (22.0–67.0)  $\mu$ g/g, respectively (Ordóñez et al. 2003).

Metal contamination was determined in soil samples collected from 10 locations in the Hafr Al Batin Area (Saudi Arabia) near the Saudi/Kuwaiti border following the Gulf War (1990–1991) (Sadiq et al. 1992a). Oil burning in Kuwait, atmospheric fallout of particulates form the use of explosives in the Gulf War, and other war-related ground activities created air pollution problems in the countries neighboring Kuwait. Vanadium concentrations in soil ranged from 2 mg/kg collected at the most distant sampling site from the Kuwaiti border (15–25 cm depth) to 59 mg/kg collected from a sampling site near the border (0–5 cm depth). Vanadium concentrations in soil samples were found to decrease with increasing distance from the border (Sadiq et al. 1992a). Various metal concentrations were determined in 25 surface soil samples from Surat, India, an industrial area. Vanadium concentrations ranged from 141.9 to 380.6 mg/kg with a mean 284.8 mg/kg (Krishna and Govil 2007).

Mean vanadium concentration of 44 and 82 mg/kg were reported in the sediments of Lake Huron and Lake Superior. Vanadium was detected in sediment samples from the Georgian Bay and North Channel (Lake Huron) at mean concentrations of 67 and 66 mg/kg, respectively (International Joint Commission 1978). Heit et al. (1984) reported vanadium concentrations in Rocky Mountain Lake sediments of

#### 6. POTENTIAL FOR HUMAN EXPOSURE

27.3 and 15 mg/kg dry weight in Lake Husted surface (0–2 cm) and subsurface sediments, respectively, and 35 and 32.8 mg/kg dry weight in Lake Louise surface and subsurface sediments, respectively. Vanadium concentrations of 55 and 43 mg/kg dry weight were reported in surface sediments from Lake Haiyaha and The Loch, two other Rocky Mountain lakes. Total vanadium concentrations of 136 and 222 mg/kg dry weight were reported in sediment samples from the Texas City channel and Ashtabula River, Ohio (Engler 1979).

Four sediment cores collected January 1996 from Central Park Lake New York City, New York were analyzed for various metals including vanadium; average vanadium concentrations ranged from 87  $\mu$ g/g at a depth of 44–47 cm to 665  $\mu$ g/g at a depth of 12–14 cm (Chillrud et al. 1999). In 1966, approximately 35% of the residual fuel oil used in New York City was from Venezuela. Vanadium is enriched in the sulfur-rich petroleum from Venezuela. Comparison of the approximate year of deposition to vanadium concentration in the sediment for Central Park Lake showed that vanadium levels in sediments from Central Park Lake were found to decrease after restrictions on sulfur content of fuel oils used in New York City were introduced starting in 1966. The average vanadium concentration peaks at 665  $\mu$ g/g in sediments from 12 to 14 cm depth, which correlates with approximately with the mid 1960s (Chillrud et al. 1999). Trace metal concentrations were measured in sediment cores collected in February 1992 from the Gulf of Mexico; the average vanadium concentrations were measured in sediment collected during early and late autumn of 1993 and 1994 from 16 locations in Lake Erie, the Niagara River, and Lake Ontario; vanadium concentrations ranged from 6.0 to 31.1  $\mu$ g/kg dry weight in these sediment samples (Lowe and Day 2002).

Vanadium concentrations in surface sediments collected during 1988–1991 from the Great Astrolabe Lagoon, Fiji ranged from 2 to 726 mg/kg dry weight. This lagoon, which encompasses a number of small volcanic islands, is considered to be a pristine marine environment with minimal human impact in this study (Morrison et al. 1997).

A diesel oil spill occurred in April 2002 from a pipeline on the Pacific side of Mexico, in Salina Cruz into the San Pedro stream, Xadani estuary, and the Superior Lagoon mouth (Salazar-Coria et al. 2007). Vanadium concentrations in sediment collected after the spill during the dry and rainy seasons were 110.5 and 123.0 mg/kg dry weight at the San Pedro site, 95.4 and 148.9 mg/kg dry weight at the Piedra Estuary, 113.3 and 107.7 mg/kg dry weight at the Xadani estuary, and <5.0 mg/kg dry weight at Superior

Lagoon, respectively. Vanadium concentrations in a reference site, upstream from the spill were below the limit of detection, <5.0 mg/kg dry weight.

Chemical contamination was measured in sediment from the Shuaiba Industrial Area (SIA), a coastal area in Kuwait that receives industrial effluent (Beg et al. 2001). The SIA contains a petrochemical company, three refineries, two power desalination plants, a melamine company, an industrial gas corporation, a paper products company, and other smaller industrial plants, as well as a large harbor. Vanadium concentrations were reported to range from 9.8 to 146.0 mg/kg dry weight in sediment from Shuaiba coastal area (Beg et al. 2001).

## 6.4.4 Other Environmental Media

The majority of foods have naturally occurring low concentrations of vanadium, many of them  $\leq 1 \text{ ng/g}$  (Byrne and Kosta 1978). Food items containing the highest levels of vanadium include ground parsley (1,800 ng/g dry weight), freeze-dried spinach (533–840 ng/g), wild mushrooms (50–2,000 ng/g dry weight), and oysters (455 ng/g wet weight) (Byrne and Kosta 1978). Intermediate levels are found in food types such as certain cereals (ranging from 0.7 ng/g in maize to 30 ng/g in Macedonian rice), fish (ranging from 3.5 ng/g in mackerel to 28 ng/g in freeze-dried tuna), and liver (ranging from 7.3 ng/g in beef to 38 ng/g in chicken) (Byrne and Kosta 1978). In general, seafoods have been found to be higher in vanadium than terrestrial animal tissues (WHO 1988). Vanadium concentrations in cow milk ranging from about 0.2 to 10 µg/kg also have been reported in older reports from the late 1970s and early 1960s, respectively (Lagerkvist et al. 1986). Pennington and Jones (1987) surveyed 234 foods from a 1984 collection of the FDA's Total Diet Study for various trace elements including vanadium. Sixty-four percent of the Total Diet Foods had vanadium concentrations of <0.5 µg/100 g and 88% had vanadium concentrations of <2 µg/100 g. Foods with the highest vanadium concentrations included breakfast cereals, canned fruit juices, fish sticks, several vegetables, sweeteners, wine, and beer. The data from this survey are summarized in Table 6-3.

Vanadium, as elemental vanadium or vanadyl sulfate, also may be found in various commercial nutritional supplements and multivitamins; vanadium concentration can range from 0.0004 to 12.5 mg in these supplements depending on the serving size recommended by the manufacturer (NLM 2009). Vanadium has been used in supplements for individuals with diabetes; intakes of 30–150 mg/day for vanadyl sulfate (9–47 mg V/day) and 125 mg/day for sodium metavanadate (52 mg V/day) have been reported (IOM 2001; Smith et al. 2008).

	Mean	Range	
Food item	(μg/100 g)		
Adult foods			
Milk, yogurt, and cheese	0.1	0–0.6	
Meat, fish, and poultry	1.0	0–11.9	
Eggs	0.3	0.2–0.4	
Nuts	0.6	0.2–1.0	
Legumes	0.1	0–0.3	
Grains and grain products	2.3	0–14.7	
Fruits and fruit juices	0.6	0–7.1	
Vegetables	0.6	0–7.2	
Mixed dishes and soups	0.6	0–2.0	
Desserts	0.9	0–2.9	
Sweeteners	2.3	0.4–4.7	
Fats and sauces	0.3	0–0.6	
Beverages	0.7	0–3.3	
Infant foods			
Formulas	0.1	0–0.2	
Meat and poultry	0.5	0–0.8	
Cereals	1.6	1.2–2.0	
Fruit and juices	1.6	0–13.4	
Vegetables	0.4	0–1.1	
Mixed dishes	0.2	0–0.6	
Custard	0.2	No data	

## Table 6-3. Vanadium Levels in Food

Source: Pennington and Jones 1987

Gummow et al. (2005) reported a study that looked at the commonly consumed tissues and milk concentrations of vanadium in cattle in South Africa that were extensively farmed over a 5-year period (1999–2004) in an area adjacent to a vanadium processing plant that was known to have higher-thannormal background levels of vanadium. The group of cattle included two groups, one group of 10 cattle that was farmed adjacent to the mine, with an average exposure of 1,229 mg V/day, and another group of 20 cattle that was farmed 2–3 km from the first group with an exposure about half that of the high exposure group (mean=532 mg V/day). Cattle in the trial were monitored over a 5-year period and six cohorts of animals were slaughtered over this period. Concentrations of vanadium in commonly consumed tissues (liver, kidney, fillet, and triceps) ranged from <0.05 to 11.51 mg/kg (wet-weight) in triceps and liver, respectively, over both groups. The median concentration of vanadium in milk was 0.23 mg/kg (range: <0.05–1.92 mg/kg) over both groups. Concentrations of vanadium in tissues from the group raised adjacent to the mine and those raised 2–3 km away were not differentiated in the presentation of the data.

Concentrations of various metals, including vanadium, were measured in samples of six fish species collected during 1997 and 1998 along the coast of the Adriatic Sea. Vanadium concentrations ( $\mu$ g/kg fresh weight) were 45.3–74.4 (anchovy), <4.0–4.8 (angler), <4.0 (hake), 6.7–29.8 (mackerel), 11.8–32.4 (red mullet), and <4.0–2.9 (sole) (Sepe et al. 2003).

Vanadium is found in almost all coals used in the United States, with levels ranging from extremely low to 10 g/kg (Byerrum et al. 1974; WHO 1988). Eastern U.S. coal has an average content of 30 ppm, western coal has an average content of 15 ppm, and coal from the interior contains an average of 34 ppm (Byerrum et al. 1974). The average vanadium content of bituminous and anthracite coal is 30 and 125 ppm, respectively (Byerrum et al. 1974).

Vanadium is usually the most abundant trace metal found in petroleum samples (Amorim et al. 2007). Vanadium concentrations in petroleum may be as high as 1,500 mg/kg, while some crude oils contain <0.1 mg/kg. Vanadium occurs predominantly as the vanadyl ion ( $VO^{2+}$ ) in the form of organometallic complexes with porphyrins. Vanadyl porphyrins originated from the formation of crude oil; the vanadyl ion was substituted for magnesium ion ( $Mg^{2+}$ ) in the chlorophylls of plants. Other vanadium complexes in petroleum include non-porphyrin and organic acid complexes (Hovmand et al. 2008). Mamane and Pirrone (1998) reported that residual fuel oils manufactured from U.S. crude oils contain 25–50 ppm of vanadium. Venezuelan, Middle Eastern, and North African residual oils have vanadium concentrations of

200–300, 10–20, and 50–90 ppm, respectively. Vanadium is highly enriched relative to other elements in heavy fuel oils due to vanadium porphyrins. Because of this, vanadium is used as a marker for emissions from fuel oil combustion (Mamane and Pirrone 1998).

Vanadium concentrations ranging from 0.49 to 5.33  $\mu$ g/g were measured in 45 different brands of whole unsmoked cigarettes. Mean vanadium concentrations of 1.11, 0.67, 0.09, and 0.33  $\mu$ g/cigarette in whole unsmoked cigarettes, ash, filter, and smoke of six different brands of cigarettes, respectively (Adachi et al. 1998a).

## 6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Food is the main source of vanadium intake for humans (Lagerkvist et al. 1986). Higher dietary intake levels are possible when food is grown in soil contaminated with greater than background levels of vanadium. Vanadium in food is mainly ingested as VO<sup>2+</sup> (vanadyl, V<sup>4+</sup>) or HVO<sub>4</sub><sup>2-</sup> (vanadate) (Sepe et al. 2003). Byrne and Kučera (1991) reported a daily intake of vanadium of 10–20  $\mu$ g. The dietary intake of vanadium estimated from the combined total intake of solids and liquids from a dietary study in EPA Region V (Indiana, Illinois, Michigan, Minnesota, Ohio, and Wisconsin) for the NHEXAS was 0.34  $\mu$ g/kg of body weight/day (Thomas et al. 1999). Pennington and Jones (1987) surveyed 234 foods from a 1984 collection of the FDA's Total Diet Study for various trace elements including vanadium. Based on this survey, estimated daily intakes of vanadium ranged from 6.2  $\mu$ g/day for 60–65-year-old females to 18.3  $\mu$ g/day for 25–30-year-old males. Table 6-4 summarizes the estimated daily intakes of vanadium for the various age groups in this study.

Various metal concentrations were determined in foods (meat, fish and seafood, pulses [lentil, bean], cereals, vegetables, fruits, tubers, whole milk, yogurt, eggs, and sugar) purchased from local markets, supermarkets, and grocery stores in zones of Tarragona County (Catalonia, Spain) near a hazardous waste incinerator, which has been operating since 1999 (Bocio et al. 2005). A dietary intake for vanadium of 28.9  $\mu$ g/day was estimated for an average adult man (70 kg body weight) in Tarragona County (Catalonia, Spain). Fish and seafood (hake, sardine, and mussels) were the only foods that contributed to this value; vanadium was not detected in any other foods that were surveyed. The detection limit for vanadium in this study was 0.25  $\mu$ g/g (Bocio et al. 2005). Sepe et al. (2003) reported an 11–34% contribution to the daily vanadium ingestion from fish collected during 1997 and 1998 along the coast of the Adriatic Sea for the population in this area.

Age group	Intake (µg/day)	
6–11 Months	6.7	
2 Years	6.5	
14–16 Years, female	7.1	
14–16 Years, male	11.0	
25–30 Years, female	8.1	
25–30 Years, male	18.3	
60–65 Years, female	6.2	
60–65 Years, male	10.6	

# Table 6-4. Estimated Daily Vanadium Intake

Source: Pennington and Jones 1987

#### 6. POTENTIAL FOR HUMAN EXPOSURE

Gummow et al. (2005) estimated dietary intakes of vanadium from the consumption of cattle in South Africa that were raised over a 5-year period (1999–2004) in an area adjacent to a vanadium processing plant that was known to have higher-than-normal background levels of vanadium. The median potential daily intakes of vanadium in the diet of humans consuming beef from these cattle were estimated to be 1.9, 1.8, 2.9, and 1.2  $\mu$ g/kg body weight/day for consuming fillet, triceps, liver, and kidney, respectively. The median potential daily intake of vanadium from drinking milk of these cattle was estimated to be 4.6  $\mu$ g/kg body weight/day (Gummow et al. 2005).

As compared to food, drinking water is a less important source of vanadium exposure for the general population. Thomas et al. (1999) reported mean vanadium concentrations of 1.2 and 1.0  $\mu$ g/L in flushed tap water and standing tap water samples from Indiana, Illinois, Michigan, Minnesota, Ohio, and Wisconsin, respectively. Assuming a daily intake of 2 L of water (EPA 1988), a daily intake of approximately 2  $\mu$ g of vanadium from tap water can be estimated.

Vanadium is present in many dietary supplements, including multivitamin and mineral supplement formulations, as well as products marketed for weight control, bodybuilding, and diabetes control (NTP 2008). The National Library of Medicine's (NLM's) Dietary Supplements Label Database lists >100 products containing vanadium (NLM 2009). Many of these products contain <10  $\mu$ g of vanadium. Some of these products contain up to 12.5 mg of vanadium depending on the serving size recommended by the manufacturer. Three containing vanadyl sulfate are also listed on the NLM's Dietary Supplements Label Database, containing 0.01–1.66 mg of vanadyl sulfate (0.003–0.52 mg vanadium) depending on the serving size recommended by the manufacturer (NLM 2009). According to the Third National Health and Nutrition Examination Survey on supplement use of vanadium, the median intake of supplements to individuals with diabetes. Intakes of 30–150 mg/day for vanadyl sulfate (9–47 mg V/day) and 125 mg/day for sodium metavanadate (52 mg V/day) have been reported (IOM 2001; Smith et al. 2008). Vanadyl sulfate supplements have been used as well by weight training athletes at levels up to 60 mg/day (18.6 mg V/day) (Barceloux 1999). Consumption of some vanadium-containing supplements may result in intakes of vanadium that would exceed those from food and water.

The general population may also be exposed to airborne vanadium through inhalation, particularly in areas where use of residual fuel oils for energy production is high (Zoller et al. 1973). Assuming air concentrations of approximately 50 ng/m<sup>3</sup>, Byrne and Kosta (1978) estimated a daily intake of 1  $\mu$ g vanadium, assuming an average inhalation rate of 20 m<sup>3</sup>/day. In addition, cigarette smoke can contribute

#### 6. POTENTIAL FOR HUMAN EXPOSURE

vanadium exposure. Koutrakis et al. (1992) estimated an emission rate for vanadium from cigarette smoke of 373 ng/cigarette; approximately 0.04 µg of vanadium is released in the smoke of one cigarette.

Lin et al. (2004) reported vanadium concentrations in the blood of 52 Taiwanese college students (19– 42 years old). None of these students had occupational exposure to vanadium and five of the students (all male) were smokers. The average vanadium concentration in was 0.42 ng/mL in all students, with a range of 0.01–1.20 ng/mL. The average vanadium concentration in blood for the female students was 0.37 ng/L and the average concentration for nonsmoking male students was 0.44 ng/L; the average for the five smokers was 0.47 ng/mL. Concentrations of vanadium in human blood reported in the literature range from 0.032 to 0.095 ng/mL (Kučera et al. 1992; Lin et al. 2004; Sabbioni et al. 1996). The average vanadium concentration in blood of individuals that have occupational exposure is 33.2 (3.10-217) ng/mL (Lin et al. 2004). Sabbioni et al. (1996) surveyed the literature for reports on vanadium determination in human blood, serum, and urine and reported that vanadium concentrations in blood and/or serum ranged from 0.45–18.4 nmol/L (0.022–0.937 µg/L) and concentrations in urine ranged from 4.16–15.7 nmol/L (0.212–0.800 µg/L). Normal concentrations of vanadium in blood and serum were reported to be around 1 nmol/L (0.05  $\mu$ g/L) and around 10 nmol/L (0.5  $\mu$ g/L) for urine. Nixon et al. (2002) reported similar values for vanadium concentrations of 0.05 and 0.24  $\mu$ g/L in serum and urine, respectively, in healthy individuals from a literature survey. Vanadium concentrations ranging from 30 to 160 µg/kg have been reported in hair (Fernandes et al. 2007; Kučera et al. 1992). No functional role for vanadium in higher animals or humans has been identified (IOM 2001).

## 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).

Similar to adults, dietary intake of vanadium through the ingestion of food is the primary exposure route for children. This route of exposure is particularly relevant when the food is contaminated with soil because soil contains an average of about 10,000 times as much vanadium as is found in many biological materials (Byrne and Kosta 1978). Since young children tend to ingest soil and dust during daily activities, children may be exposed to vanadium through the ingestion of soil or dust. Cigarette smoke can contribute vanadium exposure of children. Approximately 0.04  $\mu$ g of vanadium is released in the smoke of one cigarette (Koutrakis et al. 1992).

Blood and hair samples were collected from 23 children living in the vicinity of a metallurgical plant producing vanadium pentoxide ( $V_2O_5$ ) approximately 20 km from Prague, Czechoslovakia (Kučera et al. 1992). These children may have been exposed to vanadium due to contamination of well water. A control group consisted of 17 children from a nonpolluted rural area about 30 km from Prague. Median vanadium concentrations in hair samples from the exposed and control groups did not differ significantly, and were 98 and 88 µg/kg, respectively. The median vanadium concentration in the blood of the exposed children and the children in the control group were 0.078 and 0.042 µg/L, respectively, and were considered significantly different (Kučera et al. 1992).

Concentrations of vanadium in human breast milk of 0.46, 0.27, 0.21, 0.11, 0.69, and 0.13  $\mu$ g/g have been reported in samples from Nigeria, Zaire, Guatemala, Hungary, Philippines, and Sweden, respectively (Nriagu et al. 1992). Ikem et al. (2002) reported mean vanadium concentrations of 0.001, 0.002, and 0.003  $\mu$ g/mL in milk-based liquid formulas from the United Kingdom, milk based powdered formulas from the United States, respectively. Vanadium was not detected in milk-based powdered formulas from Nigeria and the United Kingdom. Daily intakes of vanadium for infants in the United States were estimated to be 0.05, 3.5, and 2.8  $\mu$ g/day for milk-based powder formulas, soy-based powder formulas, and hypoallergenic powder formulas from the United States, respectively (Ikem et al. 2002).

Pennington and Jones (1987) reported concentrations in infant foods that ranged from 0.1  $\mu$ g/100 g in formulas to 1.6  $\mu$ g/100 g in cereals, fruits, and juices. Daily intakes of vanadium of 6.7, 6.5, 7.1, and 11.6  $\mu$ g/day for children aged 6–11 months, 2 years, 14–16 years (female), and 14–16 years (male), respectively, were estimated based on this food survey. A summary of these data are found in Tables 6-3 and 6-4.

## 6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Populations consuming foods grown in soils supplemented with fertilizers or sludge containing vanadium or in soils naturally high in vanadium content may be exposed to concentrations higher than background levels. This is due primarily to surface deposition.

Populations in areas with high levels of residual fuel oil consumption may also be exposed to abovebackground levels of vanadium, both from increased particulate deposition upon food crops and soil in the vicinity of power plants and higher ambient air levels (Zoller et al. 1973). Cities in the northeastern United States frequently fall into this category, where ambient air levels often range from 150 to 1,400 ng/m<sup>3</sup> (Zoller et al. 1973).

Personal exposure measurements were conducted on 18 boilermakers and 11 utility workers before and during a 3-week overhaul of a large oil-fired power plant (Liu et al. 2005). Utility workers included mechanics, welders, laborers, painters, precipitator operators, work crew supervisors, and laboratory workers. During the overhaul, boilermakers worked both inside and outside the boiler and were more likely to be exposed to ash. Utility workers worked outside the boiler in adjacent areas and had little direct contact with the ash. Time-weighted average exposures for the boilermakers and the utility workers were 1.20 and  $1.10 \,\mu g/m^3$ , respectively, before the overhaul work and 8.9 and  $1.4 \,\mu g/m^3$ , respectively, during the overhaul work (Liu et al. 2005). Another study of 32 boilermaker workers found significant differences between pre- and post-shift urinary vanadium (creatinine adjusted) levels (Kim et al. 2003). Elevated vanadium levels have also been found in the nasal fluid of boilermakers, as compared to utility workers (Woodin et al. 1998).

Full-shift, personal breathing sampling was conducted on nine employees working in the finishing and cut-off areas (torch cutting, pneumatic hammer, water blast, and the five finishing workstations) of a titanium investment casting plant in Redmond, Oregon during July 7–10, 2003. Respirable vanadium pentoxide concentrations ranged from 0.0005 to 0.0089 mg/m<sup>3</sup>, with the highest measurement of 0.123 mg/m<sup>3</sup> in the torch cutting area (NIOSH 2004).

Vanadium, as elemental vanadium or vanadyl sulfate, may be found in various commercial nutritional supplements and multivitamins; vanadium concentration can range from 0.0004 to 12.5 mg in these supplements depending on the serving size recommended by the manufacturer (NLM 2009). Vanadium supplements have be used and studied as supplements for diabetic individuals. Intakes of 30–150 mg/day

for vanadyl sulfate (9–47 mg V/day) and 125 mg/day for sodium metavanadate (52 mg V/day) have been reported (IOM 2001; Smith et al. 2008). Vanadyl sulfate supplements have been used as well by weight training athletes at levels up to 60 mg/day (18.6 mg V/day) (Barceloux 1999). Consumption of some vanadium containing supplements may result in intakes of vanadium that would exceed that from food and water.

## 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 vanadium 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 vanadium.

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.** The physical and chemical properties of vanadium and its compounds are reasonably well documented (see Tables 4-1 and 4-2). No data needs are indentified.

**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 2009, became available in March of 20011. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Companies involved in the vanadium production industry (see Table 5-3), uses of vanadium and various vanadium compounds (Lide 2008; USGS 2012), and various sources of release are also available (see Table 6-1). There is little information available describing the amounts of vanadium consumed in each

use category or the quantities recycled and disposed of within the United States. Few details were found regarding the specific disposal methods used (HSDB 2009; USGS 2012). Information in each of these areas would provide an indication of the potential for human exposure as a result of disposal practices.

**Environmental Fate.** The relative contributions of natural (Byerrum et al. 1974; Zoller et al. 1973) and anthropogenic sources (Byerrum et al. 1974; TRI09 2011) of vanadium to the different environmental media are available. Partitioning between the various media is described, in particular from soil to water and from water to sediment (Wehrli and Stumm 1989; WHO 1988), but specific coefficients are not available in many studies. Information on the transport of vanadium within each media is available (Duce and Hoffman 1976; Martin and Kaplan 1998; Wehrli and Stumm 1989; WHO 1988; Zoller et al. 1973).

**Bioavailability from Environmental Media.** Occupational studies on the uptake of vanadium via the inhalation route exist; however, data suggesting that this route is relevant with regard to hazardous waste sites are lacking. Dermal absorption data are limited; however, it is likely that absorption via this route is low since vanadium, like other metals, has low solubility in lipids (WHO 1988). The daily intakes of vanadium from air, food, and water are generally small (Bocio et al. 2005; Thomas et al. 1999; Zoller et al. 1973). Seafood or milk from cows raised in an area with vanadium contamination can be a more significant dietary contribution of vanadium (Gummow et al. 2005; Sepe et al. 2003). No data needs are identified.

**Food Chain Bioaccumulation.** The uptake of vanadium in aquatic plants and animals is reasonably well documented; levels of vanadium present in different species have been established (Byerrum et al. 1974; WHO 1988). Levels present in terrestrial plants (Byerrum et al. 1974; Cannon 1963) and animals (Van Zinderen Bakker and Jaworski 1980; WHO 1988) have been established for several species. Uptake of vanadium by terrestrial plants grown on sludge-amended, or vanadium-containing fertilized fields has been studied. Vanadium does not appear to concentrate in above-ground portions of terrestrial plants (Byerrum et al. 1974). No data needs are identified.

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

Estimates of human exposure to vanadium from food (Bocio et al. 2005; Byrne and Kosta 1978; Byrne and Kučera 1991; Gummow et al. 2005; Pennington and Jones 1987; Sepe et al. 2003; Thomas et al. 1999; WHO 1988), drinking water (USGS 2009a; Lagerkvist et al. 1986; Thomas et al. 1999), and air (Byrne and Kosta 1978) are limited. Current information on emission levels from the combustion of residual fuel oil would enable a more complete picture of populations potentially exposed to higher than background ambient air levels. A data need is identified regarding vanadium levels found in environmental media in the vicinity of hazardous waste sites.

**Exposure Levels in Humans.** Limited information was located describing levels of vanadium present in human tissues for the general population (Byrne and Kosta 1978; Fernandes et al. 2007; Kučera et al. 1992; Lin et al. 2004; Nixon et al. 2002; Sabbioni et al. 1996). Little information is available on tissue levels found in populations near hazardous waste sites. A data need for vanadium levels in blood samples of the general population and those residing near hazardous waste sites is identified.

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

**Exposures of Children.** Measurements of the vanadium in blood and hair of children who have been exposed to vanadium, as well as unexposed children, are limited (Kučera et al. 1992). Additional information monitoring vanadium concentrations in children are needed. Specific data on the intake of vanadium from food eaten by children and from their diet are also limited (Ikem et al. 2002; Pennington and Jones 1987).

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

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

## 6.8.2 Ongoing Studies

No long-term research studies on the environmental fate of vanadium were identified. No ongoing studies or long-term research concerning occupational or general population exposures to vanadium were identified.