

## 5. POTENTIAL FOR HUMAN EXPOSURE

### 5.1 OVERVIEW

Vanadium is a white to gray metal with compounds widely distributed at low concentrations in the earth's crust. The average concentration of vanadium compounds in the earth's crust is 150 mg/kg. Elemental vanadium does not occur in nature, but its compounds exist in over 50 different mineral ores and in association with fossil fuels, It has six oxidation states (1-, 0, 2+, 3+, 4+, and 5+) of which 3+, 4+, and 5+ are the most common. The ion is generally bound to oxygen.

Vanadium is released naturally to air through the formation of continental dust, marine aerosols, and volcanic emissions. Anthropogenic sources include the combustion of fossil fuels, particularly residual fuel oils, which constitute the single largest overall release of vanadium to the atmosphere. These releases are generally in the form of vanadium oxides and contribute approximately two-thirds of atmospheric vanadium. 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.

The general population is exposed to background levels of vanadium primarily through ingestion of food. Workers in industries processing or using vanadium compounds are commonly exposed to higher than background levels via the inhalation pathway. The most recent estimate by NIOSH indicates that in 1980 about 5,319 people were exposed to vanadium pentoxide in their workplace. Exposure through inhalation may also be of importance in urban areas 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, however, there is little information regarding relevant or significant exposure pathways under these circumstances.

EPA has identified 1,177 NPL sites; vanadium has been found at 23 of the sites. However, we do not know how many of the 1,177 NPL sites have been evaluated for this chemical. As more sites are evaluated by EPA, this number may change (View 1989). The frequency of these sites within the United States can be seen in Figure 5-1.

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**5.2 RELEASES TO THE ENVIRONMENT**

According to the SARA Section 313 Toxics Release Inventory (TRI87), an estimated total of 78,588 pounds of vanadium were released to the environment (air, water, and land from manufacturing and processing facilities in the United States in 1987 (TRI 1989). The TRI87 data must be viewed with caution since these data represent first-time, incomplete reporting of estimated releases by these facilities. Only certain types of facilities were required to report. This is not an exhaustive list.

Releases to the environment from U.S. facilities that manufactured or processed vanadium and its compounds in 1987 are listed in Table 5-1.

**5.2.1 Air**

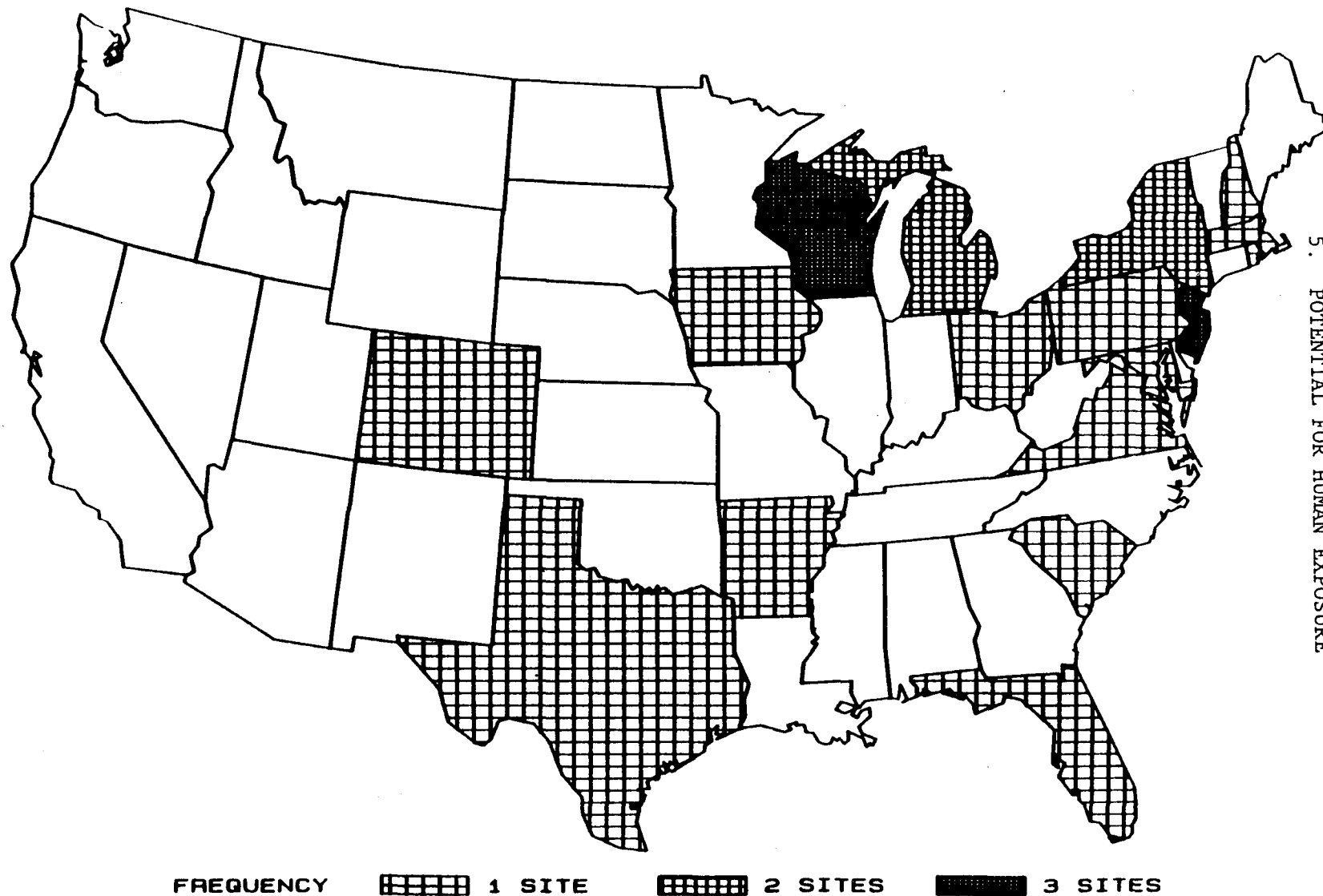
Natural sources of atmospheric vanadium include continental dust, marine aerosol, and volcanic emissions (Byerrum et al. 1974; Van Zinderen Bakker and Jaworski 1980; Zoller et al. 1973). The quantities entering the atmosphere from each of these sources are uncertain; however continental dust is believed 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).

Anthropogenic releases of vanadium to the air account for approximately two-thirds of all vanadium emissions (Zoller et al. 1973). According to TRI87, an estimated total of 20,702 pounds of vanadium were released to the atmosphere from manufacturing and processing facilities in the United States in 1987 (TRI 1989). The limitations of the estimate generated by this database, as discussed in Section 5.2, must be kept in mind, particularly as the largest anthropogenic releases of vanadium to the atmosphere are attributed to the combustion of residual fuel oils and coal, which are probably not included in the TRI87 database. These limitations are further emphasized by the fact that in 1968, the United States combustion of coal alone released an estimated 1,750 tons of vanadium oxides into the atmosphere. Other estimates for 1968 have attributed as much as 3,760 tons to this source (Byerrum et al. 1974). Furthermore, estimates of emissions from the combustion of residual fuel oils in 1969 ranged from 12,400 to 19,000 tons, while in 1970 this estimate rose to 14,000-22,000 tons (Byerrum et al. 1974). Additional unquantified sources within the United States include the burning of nearly 300 coal waste piles and the burning of wood, vegetable matter, and solid wastes, although contributions from the latter three sources may be minimal (Byerrum et al. 1974).

**5.2.2 Water**

EPA's Contract Laboratory Program Statistical Database (CLPSD) indicates that vanadium has been detected in surface water at 6% and in groundwater at

**FIGURE 5-1. FREQUENCY OF NPL SITES WITH VANADIUM CONTAMINATION \***



\* Derived from View 1989

TABLE 5-1. Releases to the Environment from Facilities that Manufacture or Process Vanadium and Compounds<sup>a</sup>

Facility	Location	Total (lbs)						POTW <sup>b</sup> transfer	Off-site transfer
		Air	Underground injection	Water	Land	Environment			
Harvey Engineering & Manufacturing Company	Hot Springs, AK	180	0	0	0	180	0	0	
Vulcraft Division Of Nucor Corp.	Fort Payne, AL	0	0	0	0	0	0	4,449	
Nibco, Inc. Blytheville Division	Blytheville, AR	365	0	0	0	365	0	0	
Aerochem, Inc.	Orange, CA	0	0	0	714	714	0	17	
Union Pacific Resources Company	Wilmington, CA	300	0	0	0	300	0	6,900	
Kloppenbergs & Company	Englewood, CO	250	No Data	0	250	500	0	0	
Laclede Steel Company	Alton, IL	94	0	0	0	94	0	241	
Caterpillar Inc. Seal Ring	Peoria, IL	No Data	No Data	No Data	0	No Data	0	No Data	
Ltv Steel Company Inc.	East Chicago, IN	250	0	1	750	1,001	0	0	
New York Blower Company	La Porte, IN	0	No Data	0	0	0	0	0	
Syndicate Store Fixtures, Inc.	Middlebury, IN	0	0	0	0	0	0	0	
Dana Corporation	Syracuse, IN	0	0	0	0	0	0	No Data	
Total Petroleum, Inc.	Arkansas City, KS	0	0	0	300	300	0	14,300	
Koch Sulfur Products Company	Desoto, KS	1	No Data	0	0	1	0	0	
National-Southwire Aluminum	Hawesville, KY	1,566	0	91	0	1,657	0	0	
Browning Manufacturing Division	Maysville, KY	500	0	0	0	500	0	0	
Baltimore Specialty Steels Corporation	Baltimore, MD	500	0	500	0	1,000	0	0	
Koch Refining Company	Saint Paul, MN	140	0	0	580	720	No Data	2	
Koch Sulfur Products Company	Wilmington, NC	250	0	0	0	250	0	0	
Shieldalloy Metallurgical Corporation	Newfield, NJ	1,450	0	0	45,000	46,450	0	0	
Shieldalloy Metallurgical Corporation	Cambridge, OH	9,750	0	0	7,100	16,850	0	20,000	
Canton Drop Forge	Canton, OH	0	0	0	1,600	1,600	0	0	
Buckeye Steel Castings	Columbus, OH	500	0	0	250	750	0	1,000	
Sohio Oil Company Toledo Refinery	Oregon, OH	750	0	0	250	1,000	0	250	

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TABLE 5-1 (Continued)

Facility	Location	Total (lbs)						
		Air	Underground injection	Water	Land	Environment	POTW <sup>b</sup> transfer	Off-site transfer
Titanium Business Operation	Milwaukie, OR	43	0	0	0	43	0	8,087
Oregon Steel Mills, Inc.	Portland, OR	250	0	0	0	250	0	0
Blaw Knox Corporation	Blawnox, PA	0	0	0	0	0	0	0
Blaw Knox Equipment Division								
Lukens Steel Company	Coatesville, PA	500	0	250	0	750	0	2,730
Ajusta Buckets, Inc.	Erie, PA	250	0	0	0	250	0	0
Sharon Steel Corporation	Farrell, PA	63	0	0	0	63	0	4,511
BP Oil Company - Marcus Hook Refinery	Marcus Hook, PA	250	0	250	0	500	0	1,916
Lockheed Aeromod Center, Inc.	Greenville, SC	0	0	0	0	0	0	0
Phillips 66 Company Sweeny Refinery and Petrochemical	Sweeny, TX	2,000	0	0	0	2,000	0	50,081
Du Pont Victoria Site	Victoria, TX	0	0	0	0	0	0	0
Roanoke Electric Steel Corporation	Roanoke, VA	0	0	0	0	0	0	0
Harnischfeger Corporation	Milwaukee, WI	250	0	0	0	250	0	0
Blaw Knox Rolls	Wheeling, WV	250	0	0	0	250	0	41,000
<b>Totals</b>		<b>20702</b>	<b>0</b>	<b>1092</b>	<b>56794</b>	<b>78588</b>	<b>0</b>	<b>155484</b>

<sup>a</sup>Derived from TRI87 (1989)

<sup>b</sup>POTW -- publicly owned treatment works

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30% of 2,783 Superfund hazardous waste sites that have had samples of all media analyzed by the CLP. The geometric mean concentration of vanadium for all sites testing positive is 18 ppm and 31 ppm for surface water and groundwater, respectively (CLPSD 1989). Note that the CLPSD includes data from NPL sites only.

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.

According to TRI87, an estimated total of 1,092 pounds of vanadium were released to surface water from manufacturing and processing facilities in the United States in 1987 (TRI 1989). However, as detailed in Section 5.2, this estimate must be viewed with caution.

### 5.2.3 Soil

The CLPSD indicates that vanadium has been detected in the soil at 48% of 2,783 Superfund hazardous waste sites that have had samples of all media analyzed by the CLP. The geometric mean concentration of vanadium for all sites testing positive is 21 ppm (CLPSD 1989). Note that the CLPSD includes data from NPL sites only.

Natural releases of vanadium to soil result from weathering of rockbearing 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

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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).

According to TRI87, an estimated total of 56,794 pounds of vanadium were released to soil from manufacturing and processing facilities in the United States in 1987 (TRI 1989). However, as detailed in section 5.2, this estimate must be viewed with caution.

### 5.3 ENVIRONMENTAL FATE

#### 5.3.1 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 man-made sources almost all 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 long-range transportation (Zoller et al. 1973). Natural sources of vanadium, as well as man-made sources such as oreprocessing 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).

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

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1989). The chemical formulas of the vanadyl species most commonly reported in fresh water are  $\text{VO}^{2+}$  and  $\text{VO}(\text{OH})^+$ , and the vanadate species are  $\text{H}_2\text{VO}_4^-$  and  $\text{HVO}_4^{2-}$  (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 sorbed 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). Sorption 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 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,



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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 great 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 under reducing, saturated conditions vanadium is immobile (Van Zinderen Bakker and Jaworski 1980).

### 5.3.2 Transformation and Degradation

Vanadium is a metallic element. 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.

#### 5.3.2.1 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)

#### 5.3.2.2 Water

Vanadium entering water is generally converted from the less-soluble trivalent state to the more-soluble pentavalent state (Byerrum et al. 1974). The species of vanadium most likely to be found in sea water are  $(\text{H}_2\text{V}_4\text{O}_{13})^{4-}$ ,  $\text{HV}_4\text{O}_4^{2-}$ , and  $\text{VO}_3^-$  (Van Zinderen Bakker and Jaworski 1980). Vanadium is continuously precipitated from sea water by ferric hydroxides and organic matter (WHO 1988) and forms sediments on the seabed.

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### 5.3.2.3 Soil

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).

## 5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

### 5.4.1 Air

Levels of vanadium measured in ambient air vary widely between rural and urban locations. Concentrations measured over the South Pole ranged from 0.001 to 0.002 nanograms (ng) of vanadium per cubic meter ( $\text{m}^3$ ) (WHO 1988) and are frequently two orders of magnitude smaller than those over the ocean at middle latitudes (WHO 1988). For example, measurements taken at nine rural sites located in the Eastern Pacific averaged 0.1 ng vanadium/ $\text{m}^3$  (range 0.02-0.8 ng vanadium/ $\text{m}^3$ ). Similar measurements taken at five different rural sites in northwestern Canada were found to average 0.72 ng vanadium/ $\text{m}^3$  (range 0.21-1.9 ng vanadium/ $\text{m}^3$ ) (Zoller et al. 1973). Between the years 1965 and 1969, average ambient concentrations in rural air in the United States ranged from less than 1 to 40 ng vanadium/ $\text{m}^3$  (Byerrum et al. 1974), although some rural areas may have levels as high as 64 ng vanadium/ $\text{m}^3$  due to localized burning of fuel oils with a high vanadium content (WHO 1988).

Vanadium levels in ambient urban air vary extensively with the season (WHO 1987; Zoller et al. 1973). U.S. cities can be divided into two groups based on the levels of vanadium present. The first group of cities is widely distributed throughout the United States and is characterized by ambient air concentrations that range from 3 to 22 ng vanadium/ $\text{m}^3$  with an average of 11 ng vanadium/ $\text{m}^3$  (approximately 20 times that of remote areas). Cities in the second group, primarily located in the northeastern United States, have concentrations that range from 150 to 1,400 ng vanadium/ $\text{m}^3$  with an average of 620 ng vanadium/ $\text{m}^3$  (Zoller et al. 1973). The variation is attributed to the use of large quantities of residual fuel oil by cities in the second group for the generation of heat and electricity, particularly during winter months (Zoller et al. 1973).

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### 5.4.2 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. Measurements of vanadium in such natural fresh waters as the 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  $\mu\text{g}$  vanadium/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 levels of up to 70  $\mu\text{g}$ /L, and in Wyoming levels were found to range from 30 to 220  $\mu\text{g}$ /L (Byerrum et al. 1974). Some municipal waters have been found to contain levels of between 1 and 6  $\mu\text{g}$  vanadium/L (Van Zinderen Bakker and Jaworski 1980), although levels of 19  $\mu\text{g}$  vanadium/L have been reported in nine New Mexico municipalities (Byerrum et al. 1974).

Levels in sea water are considerably lower than those in freshwater because much of the vanadium is precipitated (Byerrum et al. 1974; Van Zinderen Bakker and Jaworski 1980). The concentrations measured usually average 1-3  $\mu\text{g}$  vanadium/L (Van Zinderen Bakker and Jaworski 1980) although levels as high as 29  $\mu\text{g}$ /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).

### 5.4.3 Soil

Vanadium is found throughout the earth's crust at an average level of 150 mg/kg. 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 mg/kg 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).

### 5.4.4 Other Environmental Media

The majority of foods have naturally occurring low concentrations of vanadium, many of them 1 mg/g or less (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

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general, seafoods have been found to be higher in vanadium than terrestrial animal tissues (WHO 1988).

Fossil fuels frequently contain vanadium. 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 ppm and 125 ppm, respectively (Byerrum et al. 1974). Vanadium is also found in crude petroleum oils; levels range from 1 to 400 g/metric ton (Byerrum et al. 1974). Content in domestic oils range from 0.1 ppm in New Mexico to 78 ppm in Montana. Venezuelan crude oils are thought to have the highest vanadium content, ranging from 0.6 ppm in San Joaquin to 1,400 ppm in Boscan (Byerrum et al. 1974).

### 5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Although vanadium concentrations in foodstuffs are generally not higher than 1 ng/g (Byrne and Kosta 1978), food is the major source of exposure to vanadium for the general population (Vouk 1979). 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, this type of exposure is of particular importance for them. For the general population as a whole, daily dietary intake has been estimated to be on the order of a few tens of micrograms (Byrne and Kosta 1978) although other estimates from earlier studies utilizing different and possibly less sensitive analytical methods have been as high as 2 mg (Schroeder et al. 1963). In a study by Byrne and Kosta (1979), the mean vanadium levels in total dietary samples obtained in a nutrition survey in five Italian towns ranged from 8 to 12  $\mu\text{g}$  (WHO 1988). Higher dietary intake levels are possible when food is grown in soil contaminated with greater than background levels of vanadium.

Drinking water is not considered to be an important source of vanadium exposure for the general population. Although concentrations may range from 0.2 to greater than 100  $\mu\text{g}/\text{L}$  (Vouk 1979), depending upon the specific geographical location, 91% of samples from the United States had values below 10  $\mu\text{g}/\text{L}$  with an average of 4.3  $\mu\text{g}/\text{L}$ , and most values appear to be around 1  $\mu\text{g}/\text{L}$  (Vouk 1979).

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  $\text{ng}/\text{m}^3$ , Byrne and Kosta (1978) estimated a daily intake of 1  $\mu\text{g}$  vanadium by the inhalation route.

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The total body pool of vanadium in the general population is estimated to be around 100  $\mu\text{g}$  (Byrne and Kosta 1978). This estimate is based upon body burden levels of 3 ng/g in bone, up to 0.2  $\mu\text{g/g}$  in blood, 0.5 ng/g in muscle, 0.7 ng/g in fat, 10 ng/g in liver, 0.7 ng/g in brain, 30 ng/g in lung, and 5 ng/g in kidney (ICRP 1975).

The National Occupational Hazard Survey (NOHS), conducted by NIOSH in 1972-1974, estimated that 2,562 workers in 333 plants were potentially exposed to vanadium pentoxide in 1970. The largest number of exposed employees worked in the stone, clay, and glass products industry, and the second largest group was involved with electric, gas, and sanitary services (NIOSH 1976).

Preliminary data from a second workplace study, the National Occupational Exposure Survey (NOES) also conducted by NIOSH in 1980-1983, indicated that 5,319 workers in 151 plants were potentially exposed to vanadium in the workplace in 1980. Of the 5,319 workers 84% were exposed specifically to vanadium pentoxide. The largest number of workers were exposed in the chemicals and allied products industry (NIOSH 1984a).

Neither the NOHS nor the NOES databases contain information on the frequency, concentration, or duration of exposure of workers to any of the chemicals listed therein. These surveys provide only estimates of the number of workers potentially exposed to chemicals in the workplace.

### 5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

The most likely pathway of vanadium exposure for the general population is the ingestion of food bearing soil residue. Thus, populations consuming foods grown in soils supplemented with fertilizers or sludge containing vanadium may be exposed to concentrations higher than background levels. This is due primarily to surface deposition. Because infants and toddlers have a tendency to ingest soil and dust during everyday activities, soil containing background or higher levels of vanadium may result in young children being exposed to greater amounts than the general population.

Populations in areas with high levels of residual fuel oil consumption may also be exposed to above background 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  $\text{ng/m}^3$  (Zoller et al. 1973).

Populations living near the 23 NPL sites known to be contaminated with vanadium also may be exposed to high levels of vanadium compounds through contact with contaminated media.

## 5. POTENTIAL FOR HUMAN EXPOSURE

## 5.7 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 the 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 or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

## 5.7.1 Data Needs

**Physical and Chemical Properties.** The physical and chemical properties of vanadium and its compounds are reasonably well documented (see Tables 3-1 and 3-2). Further information, such as partition coefficients, would be helpful in understanding the transport and transformation of vanadium in the environment.

**Production, Import/Export, Use, and Disposal.** Companies involved in the vanadium production industry (see Table 4-1), methods used in extraction and processing (Brooks 1986; Browning 1969; Byerrum et al. 1974; Grayson 1983; Weast 1969), uses of various vanadium compounds (Brooks 1986; Browning 1969; Grayson 1983; Hilliard 1987; Mackinson et al. 1978; Symanski 1983; Weast 1969), and various sources of release are well documented (see Table 5-1). Information on recent domestic production volumes, particularly since 1985; is unavailable because the information is proprietary. In addition, 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 (Dutch Safety Institute 1980; Grayson 1983; Hilliard 1987; HSDB 1990). Information in each of these areas would provide an indication of the potential for human exposure as a result of disposal practices, and a broader picture of the vanadium industry as a whole in both domestic and global contexts.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1987, became available in May of 1989. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

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**Environmental Fate.** The relative contributions of natural (Byerrum et al. 1974; Zuller et al. 1973) and anthropogenic sources (Byerrum et al. 1974) of vanadium to the different environmental media are well documented. 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. Information on the transport of vanadium within each media is documented (Duce and Hoffman 1976; Wehrli and Stumm 1989; WHO 1988; Zoller et al. 1973), however, more details regarding the transformation between the different forms of vanadium would be useful in expanding the understanding of the biogeochemical cycling of this element. Further information on the transport and transformation of vanadium in the environment would also be helpful in identifying media relevant to human exposure pathways.

**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 primary concern regarding uptake of vanadium in the vicinity of contaminated waste sites is ingestion, particularly of contaminated food, soil, or water by children playing in the area (Byrne and Kosta 1978; Vouk 1979). However, sufficient animal data exist to indicate that absorption of vanadium via this route is limited (Conklin et al. 1982; Roshchin et al. 1980). Confirmation of this conclusion by human data would be helpful, especially since children may absorb more than adults.

**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); however, more information on accumulation in root crops might be useful in identifying populations with dietary intake that exceeds background. In general, bioconcentration and biomagnification data are limited. Further information would be useful in defining dietary pathways for general population exposure, and in estimating exposures at NPL sites.

**Exposure Levels in Environmental Media.** Vanadium levels in environmental media are reasonably well documented although more recent information would enable a more accurate assessment of potential exposure levels (Byerrum et al. 1974; Byrne and Kosta 1978; Van Zinderen Bakker and Jaworski 1980; Waters 1977; WHO 1988; Zoller et al. 1973). Current information on emission levels from the combustion of residual fuel oil would

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enable a more complete picture of populations potentially exposed to higher than background ambient air levels. Further studies on the levels and forms of vanadium found in food would be helpful in narrowing the range of values observed. This would allow a better estimation of dietary exposure. Moreover, information concerning levels found in environmental media in the vicinity of hazardous waste sites would be particularly useful.

**Exposure Levels in Humans.** Information was located describing levels of vanadium present in human tissues for the general population (Byrne and Kosta 1978). Improved sensitivity of analytical techniques would enable a more accurate estimation of exposure levels. Little information is available on tissue levels found in populations near hazardous waste sites. Further investigations of this nature would be useful in identifying risks attached to higher than background exposures, particularly for the ingestion pathway. Although vanadium can be detected in urine samples, this does not appear to have been correlated with exposure levels such as might be found near hazardous waste sites.

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

### 5.7.2 On-going Studies

No long-term research studies on the environmental fate of vanadium were identified. Environmental monitoring is being conducted in conjunction with remedial investigations and feasibility studies at 23 NPL sites known to be contaminated with vanadium. This will add to the available database on exposure levels in environmental media, chemical species, fate, and transport of the compounds.

No on-going studies or long-term research concerning occupational or general population exposures to vanadium were identified.