

## 6. POTENTIAL FOR HUMAN EXPOSURE

### 6.1 OVERVIEW

Tungsten has been identified in at least 6 of the 1,662 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2005). However, the number of sites evaluated for tungsten is not known. The frequency of these sites can be seen in Figure 6-1. Of these sites, all are located within the United States.

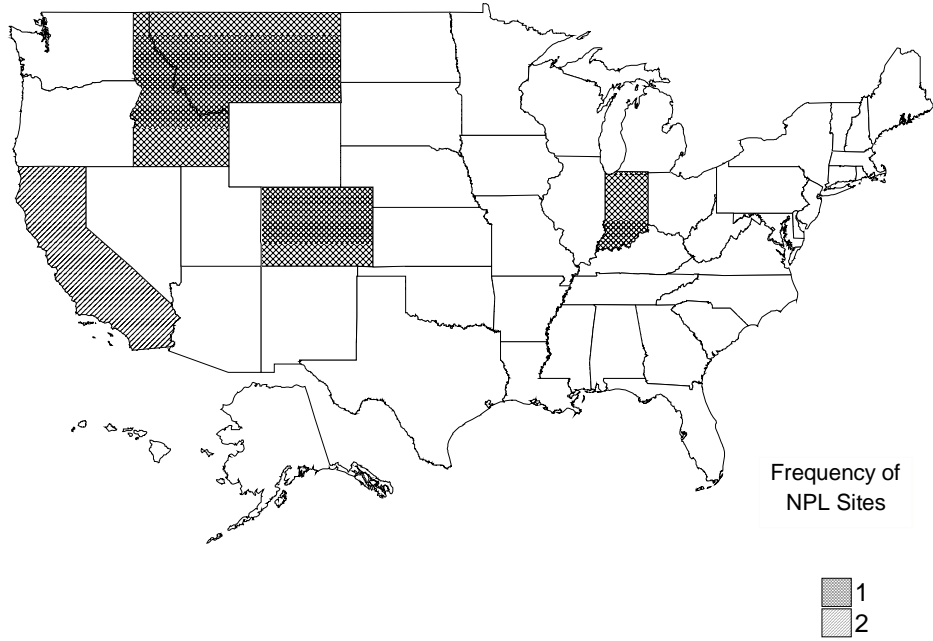
The concentration of tungsten in surface soil and streambed sediment varies by location across the continental United States. Figure 6-2 is a composite United States Geological Survey (USGS) dataset obtained using various analytical methods over many years, and shows a concentration range from <1 to >17 ppm. Though not depicted in Figure 6-2, some measured levels in Alaska exceed 24 ppm. The analysis of archived and supplemental samples using newer and more accurate techniques is enabling the USGS to produce improved maps, which currently include portions of the east coast, Alaska, Nevada, and California (USGS 2005).

Tungsten is naturally released to the atmosphere as windblown dusts. Processes of human origin, such as ore processing, hard-metal fabrication, tungsten carbide production and use, and municipal waste combustion, release tungsten to the atmosphere. Tungsten naturally enters waterways through the weathering of rocks and soils. The sources of anthropogenic releases of tungsten to surface waters include water effluents from tungsten mining and manufacturing processes. Deposition of atmospheric tungsten particulate aerosols from both natural and sources of human origin is also a source of tungsten in surface waters. Some tungsten compounds are naturally present in soil, but the concentration of tungsten in localized soils can be increased by land application of sewage sludge, fertilizers, municipal solid waste ash, and industrial wastes that contain tungsten, or deposition of atmospheric aerosols.

Atmospheric tungsten particulates will eventually settle to the earth's surface by dry deposition or may be removed from the atmosphere by wet deposition (i.e., precipitation). Upon reaching water and soil, tungsten will be in either soluble (e.g., tungstate ion,  $\text{WO}_4^{2-}$ ) or insoluble forms (e.g., tungsten trioxide) in sediment and soil. The mobility of tungsten will depend on environmental conditions such as pH. Under normal environmental conditions, tungsten is expected to have moderate to low mobility. Although chemical reactions may transform one tungsten compound into another, tungsten cannot be degraded by

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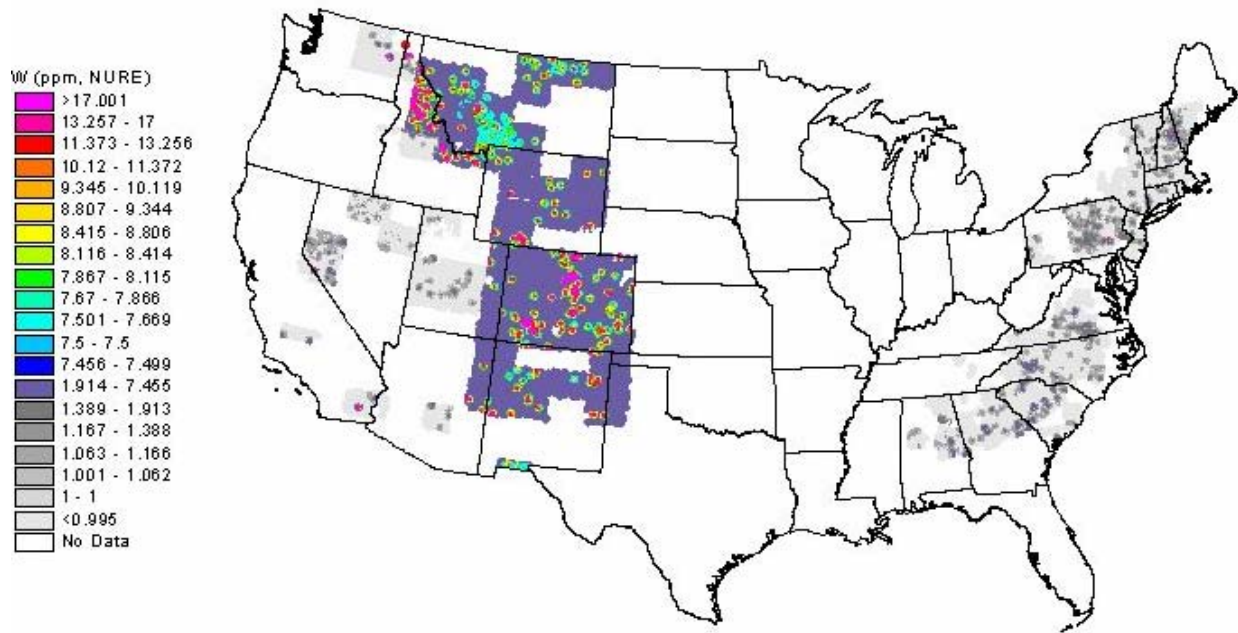
**Figure 6-1. Frequency of NPL Sites with Tungsten Contamination**



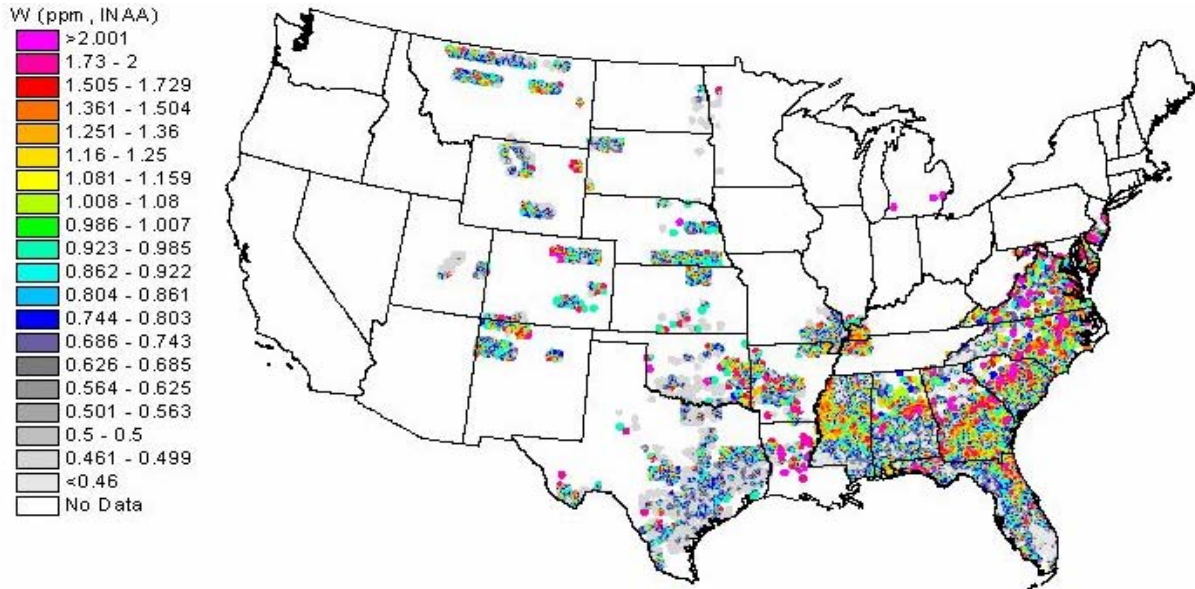
Derived from HazDat 2005

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**Figure 6-2. Tungsten Soil and Streambed Concentration Maps (USGS 2005)**



Data from the National Uranium Resource Evaluation (NURE) using a variety of analytical methods. The background coloration indicates the tungsten detection limit for analytical methods employed in a particular region. For example, violet in the west-central United States indicates that detection limits were in the range of 1.914–7.455 ppm.



Data from instrumental neutron activation analysis (INAA) showing tungsten concentrations in excess of 2 ppm along the Appalachian ridge. According to USGS (2005), the INAA method provides more accurate and uniform results than those provided by NURE. Data points are being added to provide greater map coverage.

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environmental reactions. Data regarding transformation reactions of tungsten in water and soil are limited. No information was available in the literature on the bioavailability of tungsten to plants and animals.

The concentration of tungsten in ambient air is  $<10 \text{ ng/m}^3$  (Dames et al. 1970; Haddad and Zikobsky 1985; Jagielak and Mamont-Cieřła 1979). Tungsten has not been reported in surface water or groundwater of the United States, except in areas of mineral formations containing tungsten. Tungsten is the 18<sup>th</sup> most abundant metal, having an estimated concentration in the earth's surface rocks of 1–1.3 mg/kg (Penrice 1997a). Tungsten concentrations in soils and surface soils are 0.5–83 and 0.68–2.7 mg/kg dry weight, respectively (Senesi et al. 1988). No monitoring data were located for food in the United States. Since tungsten is in soil, the absence of monitoring data for water and food indicates that analytical laboratories may not have been analyzing for this substance. Analyzing such samples using adequately low detection limits could find tungsten at measurable levels. For example, onions collected from 11 Danish sites uncontaminated by human activities other than routine agricultural practices contained tungsten at a mean level of 16.7  $\mu\text{g/kg}$  fresh weight ( $n=64$ ; range, 6.3–39  $\mu\text{g/kg}$ ) (Bibak et al. 1998).

The general population may be exposed to tungsten through inhalation of air and consumption of food. Exposure to tungsten above background levels may occur to the general population living near industries that process or use tungsten or its compounds, and to those living near hazardous sites that contain high concentrations of tungsten. However, the total tungsten intake by the general U.S. population cannot be accurately estimated due to the lack of data regarding tungsten content in food and drinking water. People who work in tungsten manufacturing, fabricating, and reclaiming industries are exposed to higher levels of tungsten and its compounds than the general population. Tungsten poses a relatively new exposure concern due to its increasing use in armor-piercing munitions and as a replacement for lead in other ammunition.

## 6.2 RELEASES TO THE ENVIRONMENT

The TRI data should be used with caution because only certain types of facilities are required to report (EPA 1997a). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the Toxics Release Inventory only if they employ 10 or more full-time employees; if their facility is classified under Standard Industrial Classification (SIC) codes 20–39; and if their facility

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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 1997a).

There is no information on releases of tungsten to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (EPA 1997a).

### 6.2.1 Air

Tungsten naturally occurs in the earth's crust and is released into the atmosphere as a result of natural processes such as entrainment of dust particles and resuspension of soil by wind. Entrainment of soil and dust particles with significant concentrations of tungsten would be most significant in areas with higher soil tungsten concentrations. Human activities, including milling and processing of tungsten and its compounds, burning of coal and municipal solid waste, and land application of fertilizers, release tungsten into the atmosphere.

Tungsten and its compounds may be emitted into the atmosphere during milling and processing operations. In the production of tungsten carbide materials for the hard-metal industry, tungsten oxide fibers were released as a by-product during the reduction stage of the raw material (Sahle et al. 1994). In 1978, Germani et al. (1981) measured an average tungsten concentration of  $15 \pm 2$  ng/m<sup>3</sup> ( $0.015 \pm 0.002$  µg/m<sup>3</sup>) in particulate emissions from five copper smelters in southeast Arizona. The concentrations of tungsten in the ore, ore concentrate, and electrostatic precipitator dust from these smelters were  $4.0 \pm 0.4$ ,  $4 \pm 1$ , and  $44 \pm 8$  µg/g, respectively.

Tungsten may be discharged into the atmosphere from the operation of urban municipal waste incineration (MWI) plants. The concentration of tungsten in fly ash from the MWI plants in Barcelona, Spain ranged from 13 to 17 µg/g in two samples (Fernandez et al. 1992). Particle-borne tungsten concentration in stack air emissions of two coal-burning units in a Western U.S. power plant ranged from 2.0 to 23.2 µg/m<sup>3</sup>. Atmospheric concentrations of particle-borne tungsten in a power plant plume were  $0.019 \pm 0.003$  µg/m<sup>3</sup>, not detected (i.e.,  $0.0050 \pm 0.011$  µg/m<sup>3</sup>) and not detected at a distance of 0–8, 8–16, and 32–64 km, respectively, from the power plant (Ondov et al. 1989). Air emissions from three different municipal waste deposits in British Columbia, Canada were sampled and analyzed for airborne tungsten compounds (e.g., tungsten carbonyl, W[CO]<sub>6</sub>). At these locations, tungsten compounds were found at concentrations ranging from 0.005 to 0.01 µg W/m<sup>3</sup> (Feldmann and Cullen 1997).

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**6.2.2 Water**

Anthropogenic and natural emissions of tungsten to water may result from mining operations and mineral weathering, respectively. Releases to surface water and groundwater typically occur in regions where natural formations of tungsten minerals are prevalent. Tungsten was found in surface water and groundwater in Northern Iceland in areas that had natural formations of tungsten minerals.

Concentrations of tungsten in these glacial and thermal waters (2–90 °C) were lower in surface water than in groundwater. Levels of tungsten were 0.03–11.5, 0.015–0.49, 0.005–0.09, 0.005–0.34, and 0.005–0.33 ppb ( $\mu\text{g/L}$ ) for groundwaters in lowland areas, groundwaters in highland areas, lakes, rivers and streams, and peat soil waters, respectively (Arnórsson and Lindvall 2001). In Japan, the concentration of tungsten was 0.67 mg/L (0.00067  $\mu\text{g/L}$ ) in river water (location not specified) polluted with liquid wastes from a tungsten mine (Mamuro et al. 1971).

Tungsten has been identified in groundwater at one site (i.e., Stringfellow, California) of the six NPL hazardous waste sites where it was detected in some environmental media (HazDat 2004).

**6.2.3 Soil**

Tungsten is naturally present in soils and sediments. Land application of sewage sludge and fertilizers containing higher than background concentrations of tungsten can be an anthropogenic source of tungsten emission to soil. Typical concentrations of tungsten in the lithosphere, parent rocks, and soil amendments such as fertilizers are listed in Table 6-1.

Military installations and areas involved in military combat operations and training may have higher concentrations of tungsten as a result of the use of military hardware containing tungsten. For example, the concentration of tungsten in surface soils samples was measured in areas of atmospheric fallout of particulates from the use of explosives in the Gulf War (1990–1991). In areas nearest to the Saudi Arabian-Kuwait border where the heaviest fall-out occurred, the maximum concentration of tungsten in soil was 126.50 mg/kg (sampling depth of 0–5 cm). In areas 300 km from the border, the concentration of tungsten was 3.25 mg/kg (sampling depth of 0–5 cm) (Sadiq et al. 1992).

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**Table 6-1. Range and Average Amounts of Tungsten in the Lithosphere, Some Parent Rocks, Some Soil-Added Materials, and Various Fertilizers<sup>a,b</sup>**

Material	Concentration (mg/kg)
Lithosphere	(0.1–2.4)
Rock phosphates and phosphorites	(30–270)
Rock carbonates	0.6
Limestones	(0.2–0.8)
Sewage sludges	(1–100)
Manure	(8–2,800)
Calcium cyanamide	0.5
Phosphate fertilizers	100
Ammonium sulfate	(ND–0.03)
Ammonium nitrate	(ND–0.20)
Calcium nitrate	0.23
Urea	(ND–0.11)
Superphosphate	3.84 (1.47–7.04)
Triple superphosphate	3.29 (1.59–4.99)
Potassium sulfate	(ND–0.75)
NP compound	1.28 (ND–3.99)
NPK compound	0.89 (0.02–2.03)

<sup>a</sup>Source: Senesi et al. (1988); detection limit = 0.002 mg/kg

<sup>b</sup>The values presented correspond also to the contribution, in g/ha, of tungsten from 1 mg of fertilizer applied to 1 ha of soil.

ND = not detected; NP = nitrogen and phosphate; NPK = nitrogen, phosphate, and potash

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Tungsten has been identified in soil at one site (i.e., Anaconda Co. Smelter, Montana) of the six NPL hazardous waste sites where it was detected in some environmental media (HazDat 2004).

### 6.3 ENVIRONMENTAL FATE

#### 6.3.1 Transport and Partitioning

Tungsten and most tungsten compounds have low vapor pressures at 25 °C and are expected to exist in the particulate phase in air (HSDB 2004; Penrice 1997b). Some exceptions are tungsten carbonyl and tungsten hexafluoride. According to a model of gas/particle partitioning of semivolatile organic compounds in the atmosphere, tungsten carbonyl, which has a vapor pressure of 0.1 mm Hg at 20 °C, is expected to exist in both vapor and particulate phases in the atmosphere (Bidleman 1988; O'Neil et al. 2001). Tungsten hexafluoride is a gas at room temperature (Lide 2000). Vapor- and particulate-phase tungsten compounds may be removed from the air by wet and dry deposition. In Norway, between the years 1993 and 1995, the mean annual wet deposition flux of tungsten ranged from 2 to 10  $\mu\text{g}/\text{m}^2$  per year (n=13) (Berg and Steinnes 1997). Tungsten-containing soil can be re-suspended into the atmosphere by wind.

In water, tungsten metal and metal alloys will exist as insoluble solids, while tungsten compounds will exist as ions or insoluble solids (Cotton and Wilkinson 1980). Tungsten compounds are expected to adsorb to suspended soils and sediment in the water column. Tungsten may be present in water as soluble tungstate ions, and also as species with inorganic colloids (Tanizaki et al. 1992). Soluble tungsten compounds (e.g., tungstates) may leach into groundwater. Volatilization from moist soil and water surfaces is not expected to be important for tungsten metal, alloys, and compounds due to their low vapor pressures (HSDB 2004; Penrice 1997b).

Tungsten is carried to rivers, lakes, and oceans by land erosion. The estimated residence time of tungsten in ocean water, as the tungstate ion ( $\text{WO}_4^{2-}$ ), before it is removed from the aquatic phase by sedimentation or other removal processes, is approximately 1,000 years (Bowen 1966).

Sorption coefficients for tungsten suggest that it is expected to have moderate to low mobility in soil under normal environmental conditions (Meijer et al. 1998). The sorption coefficient ( $K_d$ ) for tungsten increases with decreasing pH. The sorption coefficients for the tungstate ion are 100–50,000 at about



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pH 5; 10–6,000 at about pH 6.5; and 5–90 at pH 8–9 (Meijer et al. 1998). The sorption behavior of tungsten is due to changes in the surface charge of the soil as the contact solution becomes more acidic or alkaline. Tungsten combines with a large number of organic ligands (Lassner et al. 1996). However, no information on stability of tungsten organic matter complexes was located in the literature. Also, no information on the sorption of tungsten in saline environments was located in the literature.

The concentration of tungsten in plants is low (Bowen 1960). Beans were found to incorporate tungsten when grown in soil amended with 1, 5, and 10% by weight tungsten metal or tungsten trioxide powder. The uptake was higher for tungsten metal than its oxide (1,100 mg/kg for metal versus 820 mg/kg for oxide at 10% weight percent) and increased with soil concentration in an apparently asymptotic manner. Rye grass was also found to take up tungsten from soil into the plant stem (U.S. Army 2000).

No information on the bioavailability of tungsten to animals was available in the literature. Soluble forms of tungsten, such as tungstate ions, will be more bioavailable to fish and animals than insoluble forms. No evidence of the bioaccumulation of tungsten in the food chain of humans was located in the literature.

### 6.3.2 Transformation and Degradation

Degradation of an element, such as tungsten, is a nuclear process, by definition. Stable elements, such as tungsten, typically undergo such processes only at insignificant rates in the environment. As an element, tungsten cannot degrade chemically. It can change, however, from one chemical form to another, sometimes reversibly, in numerous chemical reactions that can proceed under a wide range of common environmental conditions.

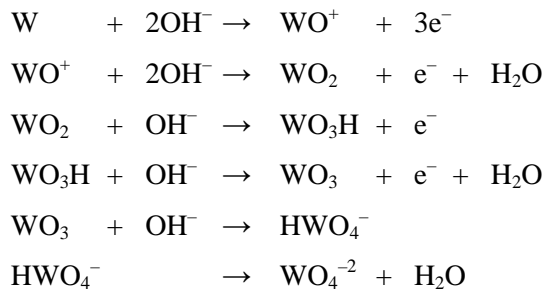
#### 6.3.2.1 Air

Insoluble particulate-phase tungsten metal, alloys, and compounds are not expected to react in air. Soluble particulate-phase compounds, such as ammonium paratungstate and tungsten hexachloride, may react with moisture in air to form tungstate ions (e.g.,  $\text{WO}_4^{2-}$ ). There is no evidence in the literature for interaction of soluble or insoluble particulate-phase tungsten with  $\text{CO}_2$  (gas) or other compounds in the atmosphere. No information was found in the literature on photooxidation or photolysis of tungsten compounds in the atmosphere.

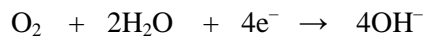
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**6.3.2.2 Water**

The reaction of tungsten in water is controlled by chemical speciation by which one species is converted to another. Tungsten exists in several oxidation states, 0, 2+, 3+, 4+, 5+, and 6+ (Bingham et al. 2001). The most stable is 6+ with the lower states being relatively unstable. Tungsten can exist as ions in water with one or more elements such as oxygen. In natural waters, tungsten is primarily in the form of the soluble tungstate ion (i.e.,  $\text{WO}_4^{2-}$ ) under alkaline conditions or other tungsten polyanions under acidic conditions (Bowen 1966; Lassner et al. 1996; Tanizaki et al. 1992). Dissolution of tungsten metal in aqueous solution likely occurs through a stepwise anodic oxidation of the metal to the  $\text{W}^{+6}$  oxidation state through the intermediate formation of the  $\text{W}^{+3}$ ,  $\text{W}^{+4}$ , and  $\text{W}^{+5}$  oxidation states, as shown in the reaction scheme below (Dermatas et al. 2004; Lassner and Schubert 1999).



The accompanying cathodic reaction involves the reduction of dissolved molecular oxygen:



The dissolution of tungsten metal typically results in the decrease of the pH of the local media (Dermatas et al. 2004). The extent and rate of tungsten dissolution changes when alloyed with other metals. Iron has been shown to enhance the dissolution of tungsten, but cobalt reduces the rate and extent of tungsten dissolution (Dermatas et al. 2004).

Tungsten has a strong tendency to form complexes; this is exemplified by the large series of heteropoly acids formed with oxides of phosphorous (e.g., phosphotungstic acid), arsenic, vanadium, silicon, and others (Bingham et al. 2001). Tungsten combines with a large number of organic ligands (Lassner et al. 1996). However, no information on natural tungsten organic matter complexes was located in the literature.

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In surface water, elevated tungsten levels may inhibit ammonification and nitrification of organic compounds and growth of saprophytic microflora (Nadeenko 1966). Experimental analysis using three different tungsten compounds (sodium tungstate, sodium phosphotungstate, or tungstic acid) revealed marked reduction in oxygen consumption at a tungsten concentration of 1 µg/L, a marginal reduction (10–20%) at 0.1 µg/L, and no significant effect at 0.01 µg/L.

**6.3.2.3 Sediment and Soil**

Typical transformation processes for tungsten in soil include precipitation, complexation, and anion exchange. Important factors affecting the transformation of tungsten in soils and sediments include pH, ionic strength (i.e., salinity), redox potential, concentration and distribution of species, composition of the mineral matrix, organic matter, and temperature. It is likely that dissolution of tungsten in soil will occur through a similar reaction process to those described for tungsten in water, resulting in a similar decrease of soil pH. Dermatas et al. (2004) have demonstrated that this lowering of soil pH can result in the death of soil organisms. Tungsten binds with soils with the extent of tungsten uptake into soils appearing to follow the order: Pahokee peat > montmorillonite >> illite > sand (Dermatas et al. 2004). High uptake of tungsten in high organic soils, such as Pahokee peat, is thought to occur through the formation of tungsten complexes with humic substances in these soils. Binding of tungsten to some soils (e.g., montmorillonite and illite) occurs through cooperative adsorption, likely through the polymerization of tungstates to form isopolytungstates (Dermatas et al. 2004). The uptake of tungsten into montmorillonite and illite soils is usually accompanied by an increase in the pH of the local media. These binding processes have the effect of limiting the mobility of tungsten in soils. Leachability and mobility tests were conducted on bullets made of tungsten or tungsten-tin powder that were pressed and crushed to simulate degradation when fired into several media (sand, soil, and mixtures containing gravel, steel plates, and concrete). The powders were mixed with soil (sand or topsoil), exposed to a leachant (deionized water, acid rain, or salt water), and leached by up-flow and hold methods. Little or no tungsten leached from the topsoil, but tungsten did penetrate the sand column and filter, indicating that small-sized particles of tungsten can be mobile in sandy soil (U.S. Army 2000). No other biotransformation studies of tungsten or its compounds were located in the literature.

**6.3.2.4 Other Media**

No data on the transformation of tungsten in other media were located in available literature.

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**6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT**

Reliable evaluation of the potential for human exposure to tungsten depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of tungsten 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 tungsten 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 tungsten in a variety of environmental media are detailed in Chapter 7.

**6.4.1 Air**

Ambient concentrations of tungsten in air have been measured at levels  $<10 \text{ ng/m}^3$  (Dames et al. 1970; Haddad and Zikobsky 1985; Jagielak and Mamont-Cieřła 1979). Between 1972 and 1976, mean values of tungsten determined for atmospheric air in Siersza (a small industrial town) and the Warsaw district of Zerań, Poland were  $5.8$  and  $4.5 \text{ ng/m}^3$ , respectively, while concentrations in dust were  $44$  and  $19 \text{ ppm}$ , respectively, for the same locations (Jagielak and Mamont-Cieřła 1979). The ambient average air concentration of tungsten in the urban air of Montréal, Quebec, Canada was  $5.2 \text{ ng/m}^3$  (Haddad and Zikobsky 1985). Dames et al. (1970) measured the concentration of tungsten in urban air at East Chicago, Indiana, an industrial area of northwest Indiana, and Niles, Michigan, which is about 50 miles to the northeast of this industrial area. The concentration of tungsten in suspended particulates from East Chicago, Indiana was  $5.8 \text{ ng/m}^3$  while the concentration in samples taken from Niles, Michigan was  $0.4 \text{ ng/m}^3$ .

Tungsten has been detected at sub-nanogram concentrations at remote locations around the world, possibly the result of natural processes such as entrainment of dust particles and resuspension of soil by wind. The average concentrations of tungsten in particles collected from the Arctic haze of the free troposphere, in the stratosphere, and in the marine boundary over various Arctic regions were as follows (Sheridan and Zoller 1989): North American Arctic,  $0.14 \pm 0.09 \text{ ng/m}^3$  ( $n=10$ ); Norwegian Arctic,  $0.073 \pm 0.031 \text{ ng/m}^3$  ( $n=9$ ); stratosphere filters,  $0.033 \pm 0.011 \text{ ng/m}^3$  ( $n=10$ ); and marine boundary layer filters,  $0.095 \pm 0.021 \text{ ng/m}^3$  ( $n=7$ ). The arithmetic mean atmospheric concentration of tungsten at the

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geographic South Pole was  $0.0015 \pm 0.0008$  ng/m<sup>3</sup> during the Austral summer of 1974–1975 (Maenhaut et al. 1979).

Tungsten levels in indoor air have been determined as part of a 1998 study of metal exposures for residents of a retirement home in Towson, Maryland (Graney et al. 2004). The study participants had a mean age of 84, were all non-smokers, and did not typically cook their own meals. Median tungsten concentrations of 0.010 and 0.007 ng/m<sup>3</sup> in air were reported in particulate matter (PM<sub>2.5</sub>) samples collected from indoor air and personal exposure samplers, respectively.

#### 6.4.2 Water

Limited data have been reported on the concentrations of tungsten in surface water and groundwater from the United States. Taylor et al. (1990) reported semi-quantitative concentrations of tungsten in river waters of the Mississippi River and its tributaries at concentrations  $\leq 0.2$  µg/L (i.e., semi-quantitative detection limit of 0.2 µg/L) with 4 of 15 samples showing positive analytical results for tungsten. These results indicate that tungsten may be present in ambient surface waters. However, semi-quantitative results should be interpreted with caution since they may not reflect actual concentration levels. In 1992, water samples were analyzed for three river systems (Truckee, Walker, and Carson, Nevada), which are in regions of natural tungsten mineral formations (Johannesson et al. 2000). The purpose of the study was to assess the interrelationships among metal and other ionic concentrations as the three rivers lost water through evaporation. In the Truckee river system, tungsten varied from a low value of 1.73 nmol/kg (0.319 µg/L) to a high value of 391 nmol/kg (72.1 µg/L). In the Walker and Carson systems, tungsten varied from 0.82 to 22.1 nmol/kg (0.15–4.07 µg/L), and from 8.21 to 1,029 nmol/kg (1.51–189.7 µg/L), respectively. The high concentration of tungsten in these rivers reflects the relative stability of the tungstate ion (WO<sub>4</sub><sup>2-</sup>) in the alkaline and well-oxygenated waters; contributions from hydrothermal waters; and weathering of rocks/regoliths with high concentrations of tungsten. Samples from these rivers may potentially be potable drinking water sources.

Limited monitoring data were located for urban environments in the United States. However, in the City of Fallon in Churchill County, Nevada, several studies have been conducted. In 2002, a mean concentration of 19.9 µg/L was determined for tungsten in tap water sampled from 76 private and municipal residential water supplies (Agency for Toxic Substances and Disease Registry 2003). Upon further analysis of the concentration data, it was found that tungsten levels were highest in water taken from private residential wells with values ranging from 0.25 to 337 µg/L and a mean value of 37.5 µg/L.

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In comparison, the tungsten concentrations were found to be lower in tap water sampled from residences using municipal water supplies, with values ranging from 0.25 to 27.2 µg/L and a mean value of 19.1 µg/L. In a study conducted by the Centers for Disease Control and Prevention (CDC) of household water supplies in the Churchill County community the concentrations of tungsten were found to range from 0 to 217.3 µg/L (CDC 2003b). However, in a follow-up study of three nearby communities, Yerington, Lovelock and Pahrump, tungsten concentrations in tap water were found to be lower, with values ranging from 0.01 to 40 µg/L, 0.02–2.0 µg/L, and 0.01–1.0 µg/L and mean (geometric) values of 3.32, 0.11 and 0.04 µg/L, respectively (CDC 2003c). No further data were located on the concentrations of tungsten in drinking water from the United States. However, according to EPA sampling and analytical methods, tungsten is not a substance that is typically measured in drinking water.

For non-U.S. locations, tungsten has been detected in surface water from urban areas. The levels of tungsten were measured in river water from the Tamagawa and Sagami Rivers located near Tokyo, Japan (Tanizaki et al. 1992a). The range of tungsten concentrations in the dissolved and suspended fractions of these samples were as follows: dissolved fraction (particulates <0.45 µm), 0.0265–0.107 µg/L; dissolved fraction (molecular weight <500), 0.0105–0.0341 µg/L; dissolved fraction (molecular weight=500–10<sup>4</sup>), 0.0141–0.0701 µg/L; dissolved fraction (molecular weight >10<sup>4</sup>), 0–8.7 ng/L; and suspended solids (particulates >0.45 µm), 0–0.104 µg/L. In river water from the Asakawa, Nogawa, and Hisasegawa Rivers and effluent from a sewage treatment plant (all located near Tokyo, Japan), the levels of tungsten were determined to range as follows: dissolved fraction (particulates <0.45 µm), 0.014–0.785 µg/L ; dissolved fraction (molecular weight <500), 0.0206–0.247 µg/L; dissolved fraction (molecular weight=500–10<sup>4</sup>), 0.0270–0.537 µg/L; dissolved fraction (molecular weight >10<sup>4</sup>), 0–0.0023 µg/L; and suspended solids (particulates >0.45 µm), 0.002–0.060 µg/L (Tanizaki et al. 1992b). Tungsten was measured in highly solute-rich river systems in a heavily industrialized region of India. Mean concentrations of tungsten in the Mahanadi, Brahmani, and Baitarani Rivers were 0.05 µg/L (range, 0.02–0.9 µg/L), 0.15 µg/L (range, 0.04–0.89 µg/L), and 0.08 µg/L (range, 0.04–0.18 µg/L), respectively (Konhauser et al. 1997).

Locations with natural formations of tungsten have elevated levels of tungsten in surface water and groundwater. The Nahanni River, a spring-fed river system in an area of scheelite/wolframite bearing minerals located in Northwest Territories of Canada, was found to contain tungsten at concentrations ranging from <0.1 to 224.5 µg/L (Hall et al. 1988). Tungsten was found in surface water and groundwater in Northern Iceland in areas that had natural formations of tungsten minerals. Concentrations of tungsten in these glacial and thermal waters (2–90 °C) were lower in surface water than

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in groundwater. Levels of tungsten were 0.03–11.5, 0.015–0.49, 0.005–0.09, 0.005–0.34, and 0.005–0.33 ppb ( $\mu\text{g/L}$ ) for groundwater in lowland areas, groundwater in highland areas, lakes, rivers and streams, and peat soil waters, respectively (Arnórsson and Lindvall 2001). Tungsten that is found in the surface water and groundwater of the Ethiopian Rift Valley is associated with thermal activity in the region. Tungsten concentrations ranged from  $<0.002$  to  $3.81 \mu\text{g/L}$  in water samples taken from deep ( $>60$  meters depth) and shallow ( $<60$  meters depth) wells, hot springs, and rivers, with a median value of  $0.011 \mu\text{g/L}$  (Reimann et al. 2003). The concentrations were lowest in water samples taken from rivers and shallow wells and highest in samples obtained from hot springs and deep wells. In a separate study of the rivers and soda lakes within the Rift Valley, tungsten concentrations ranged from  $<0.1$  to  $545.9 \mu\text{g/L}$  with the highest concentrations found in Lakes Abijata and Mechaferra (Zinabu and Pearce 2003). The high levels of tungsten and other heavy metals (e.g., As, Hg, Mo, Rb, Ti) in these lakes were attributed to a high degree of wildlife habitation in these lakes.

The concentration of tungsten in seawater is typically about  $0.1 \mu\text{g/L}$  (Bowen 1966).

Tungsten has been detected at low concentrations in rainwater near locations with tungsten emissions. Rainwater analysis performed in the United Kingdom illustrated that ambient tungsten concentrations in rainwater typically are  $<1 \mu\text{g/L}$  (Hartung 1991). Kist (1994) determined the levels of tungsten in rainwater sampled 8 km from a hard-metal factory in Russia. The concentrations of tungsten in the solid and soluble phases of rainwater were  $0.00014$  and  $0.00076 \mu\text{g/L}$ , respectively. The authors suggest that the enrichment of tungsten in the liquid phase may be explained for this area by a high concentration of tungsten as liquid aerosols and vapor-phase compounds rather than particulates.

### 6.4.3 Sediment and Soil

Tungsten is the 18<sup>th</sup> most abundant metal, having an estimated concentration in the earth's surface rocks of  $1\text{--}1.3 \text{ mg/kg}$  (Penrice 1997a). Tungsten concentrations in soils and surface soils are  $0.5\text{--}83$  and  $0.68\text{--}2.7 \text{ mg/kg}$  dry weight, respectively (Senesi et al. 1988). Agricultural soils from New Zealand had mean concentrations of tungsten ranging from  $1.9$  to  $21.4 \text{ mg/kg}$  ( $n=2$ ), while mineralized areas had tungsten concentrations ranging from  $65$  to  $125 \text{ mg/kg}$  ( $n=3$ ) (Quin and Brooks 1972a, 1972b). Fu and Tabatabai (1988) measured a mean concentration of  $0.89 \text{ mg/kg}$  (range,  $0\text{--}2 \text{ mg/kg}$ ) for agricultural soils from Iowa (Fu and Tabatabai 1988).

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**6.4.4 Other Environmental Media**

Tungsten was detected in ambient air and gas wells within three municipal waste disposal sites near Vancouver, British Columbia (Feldman and Cullen 1997). The concentration of tungsten compounds in the landfill gas collected from gas wells ranged between 5 and 10 ng W/m<sup>3</sup>. Concentrations of tungsten compounds in the ambient air over the landfills were under 1 ng W/m<sup>3</sup>. Based on mass spectrometric analysis of the gas components, the tungsten measured in the landfill gas and ambient air samples was in the form of hexacarbonyl tungsten (W[CO]<sub>6</sub>).

At Cayuga Lake, New York, tungsten was not detected in lake trout (*Salvelinus namaycush*) ranging in age from 1 to 12 years at a detection limit of 0.2 ppb fresh weight (Tong et al. 1974). Sea animals have been reported to contain tungsten in dry tissues at concentrations ranging from 5x10<sup>-4</sup> to 5x10<sup>-2</sup> mg/kg (Bowen 1966).

No monitoring data were located for food in the United States. Onions collected from 11 Danish sites uncontaminated by human activities other than routine agricultural practices contained tungsten at a mean level of 16.7 µg/kg fresh weight (n=64; range, 6.3–39 µg/kg) (Bibak et al. 1998). Blueberries and lingonberries collected from 35 urban and mining area sites in Northern Sweden from September to October 1998 contained tungsten at concentrations of 0.23–3.7 ng/g and 0.22–7.2 ng/g, respectively (Rodushkin et al. 1999). Perez-Jordan et al. (1998) semi-quantitatively determined the concentrations of tungsten in Spanish wines as follows: red-Valencia, 0.25±0.06 ng/mL; red-Utiel-Req, 0.09±0.03 ng/mL; red-Rioja, 0.55±0.05 ng/mL; white-Valencia, 0.25±0.01 ng/mL; white-Utiel-Req, 0.11±0.01 ng/mL; and white-Rioja, 0.6±0.4 ng/mL.

The concentration of tungsten in land plants ranges from 0.0005 to 0.150 mg/kg dry weight (Bowen 1960). Mean concentrations of tungsten in plants were reported as follows: source unknown from New Zealand, 0.27–39.5 mg/kg; tree leaves from New Zealand, 2.2–3.5 mg/kg; and agricultural plants from Iowa, 0.18 mg/kg (Fu and Tabatabai 1988; Quin and Brooks 1972a, 1972b). Quin and Brooks (1972b) determined the tungsten content of some native trees and ferns growing in an area of tungsten mineralization in Westland, New Zealand. The highest value reported was 1,500 mg/kg of ash weight in the leaves of black hard fern (*Blechnum nigrum*). The concentration of tungsten in tree ferns showed a significant correlation with the concentration in the soil; the tungsten content of trees did not. The mean concentration of tungsten in tree bark (oak) sampled from the western part of the Czech Republic was 0.775±0.569 mg/kg (n=389; range, 0.129–4.79 mg/kg) (Böhm et al. 1998). Freitas et al. (1988) measured



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the concentration of heavy metals in aquatic macrophytes from the Fractal Dam (Tejo River, Portugal) in March 1987. Tungsten was found in whorled-water milfoil (*Myriophyllum verticillatum*), water buttercup (*Ranunculus sp.*), and pondweed (*Potamogeton sp.*) at average levels of  $3.1 \pm 0.4$ ,  $5.6 \pm 0.2$ , and  $2.5 \pm 0.1$  ppm, respectively. Lichen (*Hypogymnia physodes L.*) sampled in Slovenia in 1992 was found to contain tungsten at a mean concentration of  $0.17 \pm 0.13$   $\mu\text{g/g}$  dry weight ( $n=82$ , range, 0.04–0.80  $\mu\text{g/g}$  dry weight) (Jeran et al. 1996). Two species of moss (i.e., *Hylocomium splendens* and *Pleurozium schreberi*) collected around Norway between the years 1993 and 1995 were found to contain tungsten at concentrations of 0.027–0.15  $\mu\text{g/g}$  ( $n=13$ ) and 0.012–0.093  $\mu\text{g/g}$  ( $n=13$ ), respectively (Berg and Steinnes 1997). In areas around Norway and Russian Kola Peninsula and Tver region, the concentrations of tungsten in moss (*H. splendens*), lichen (*Usnea sp.*), and pine needles (*Pinus sylvestris L.*) were 0.73, <0.2, and 0.34 ppm, respectively (Nazarov et al. 1995).

Tungsten concentrations in the lithosphere, some parent rocks, some soil-added materials, and various fertilizers are illustrated in Table 6–1. Sewage sludge samples from 16 major U.S. cities and Iowa contained tungsten at mean concentrations of 19.4 mg/kg ( $n=16$ ; range, 0.9–99.6 mg/kg) and 4.3 mg/kg (range, 0.5–62 mg/kg), respectively (Furr et al. 1976; Senesi et al. 1988). The mean concentration of tungsten in sewage sludge samples from 23 U.S. cities was 14.4 ppm dry weight ( $n=30$ ; range, 0.65–140 ppm dry weight) for samples collected in 1980 (Mumma et al. 1984). Municipal waste ash samples from Japan contained tungsten at median levels as follows: food scrap ash, 0.9 mg/kg (range, 0.24–1.25 mg/kg); animal waste ash, 0.8 mg/kg (range, 0.20–1.56 mg/kg); horticulture waste ash, 1.6 mg/kg (range, 0.86–3.99 mg/kg); sewage sludge ash, 11.8 (range, 5.13–21.5 mg/kg); and incinerator bottom ash, 4.4 mg/kg (range, 2.46–11.4 mg/kg) (Zhang et al. 2002).

Some types of coal may contain tungsten at significant levels. In the United States, tungsten was found in Pocahontas coal at concentrations of 0.5 and 49 ppm dry weight in the organic and sulfide fractions, respectively (Pires et al. 1997). However, it was not detected in any fraction of Davis, Colchester, Herrin, or Pittsburgh coals.

Tungsten content has been measured in slags collected from smelters located on abandoned copper and silver mines. Tungsten concentrations were found to range from 0.4 to 2.6 mg/kg in slags taken from the Ely and Elizabeth mines in Vermont and the mining district of Ducktown, Tennessee (Piatak et al. 2004). In one measurement for a slag from the Clayton silver mine in the Bayhorse mining district of Idaho, a tungsten concentration of 175 mg/kg was obtained. In the same study, it was found that tungsten was not readily leached from these slags when extracted with deionized water or an acidified extractant that

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simulated precipitation in the eastern United States. This is demonstrated in the finding that the concentration of tungsten in the extractants was at or near the limit of detection of the assay ( $<0.3\text{--}0.6\ \mu\text{g/L}$ ) for all of the slags tested.

**6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE**

Although data are limited, the general population may be exposed to trace amounts of tungsten by inhalation of air. Bowen (1966) reported a provisional dietary intake of  $49\ \mu\text{g/day}$  for tungsten for a 70-kg man with a diet of 750 g dry weight per day. Since no drinking water data are available for tungsten, an estimated daily intake from drinking water could not be estimated. However, based on limited surface water data for tungsten, the estimated daily intake from drinking water is predicted to be negligible. No information on the concentrations of tungsten in food was located in the available literature.

A National Occupational Exposure Survey conducted by NIOSH during 1981–1983 estimated the number of individuals who were potentially exposed to tungsten and its compounds in the workplace (NIOSH 1983). The total number of individuals occupationally exposed to tungsten was 47,052 (i.e., the sum of three hazard classifications). The number of individuals occupationally exposed to tungsten compounds was as follows (number in parenthesis): sodium tungstate, dihydrate (2,254); sodium tungstate, anhydrous (15,470); sodium phosphotungstate (73); and tungsten carbide (3,395).

Most exposures to tungsten and its compounds in occupational environments occur during production of tungsten metal from the ore, and preparation of tungsten carbide powders. Exposures to cemented tungsten carbide occur in manufacturing and grinding cemented tungsten carbide hard-metal parts. Dusts and mists of tungsten and its compounds or cemented tungsten carbide are produced during crushing, mixing, ball milling, loading and unloading, sintering, cutting, sandblasting, and grinding operations. Because of the high melting points of tungsten compounds, exposures to their vapors are negligible (NIOSH 1977). Table 6-2 lists occupations with potential exposure to tungsten and its compounds.

Tungsten exposure levels for individuals working in the hard-metal industry are illustrated in Table 6-3. In the United States, the breathing zone air concentration of tungsten ranged from  $0.2$  to  $12.8\ \text{mg/m}^3$  for workers involved in the wet grinding of sintered pieces without ventilation (NIOSH 1977). Schwartz et al. (1998) reported that tungsten was found in lung tissues of five individuals occupationally exposed involved in the sandblasting of hard metal tools. The effects of tungsten particulate aerosols on

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**Table 6-2. Occupations with Potential Tungsten Exposure**

Alloy makers	Melting, pouring, casting workers
Carbonyl workers	Metal sprayers
Ceramic workers	Ore-refining and foundry workers
Cemented tungsten carbide workers	Paint and pigment makers
Cement makers	Papermakers
Dyemakers	Penpoint makers
Dyers	Petroleum refinery workers
Flameproofers	Photographic developers
High-speed tool steelworkers	Spark-plug makers
Incandescent-lamp makers	Textile dryers
Industrial chemical synthesizers	Tool grinders
Inkmakers	Tungsten and molybdenum miners
Lamp-filament makers	Waterproofing makers
Lubricant makers	Welders

Source: NIOSH 1977

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**Table 6-3. Worker Exposure to Tungsten in the Hard-Metal Industry**

Type of operation	Total dust (mg/m <sup>3</sup> )	Tungsten (mg/m <sup>3</sup> )	Sample type	Location
Powder processing				
	14.9	7.7	G	Austria
	0.3–9.8	1.8–8.24	B	Switzerland
	1.1–32	0.88–25.6	B	Sweden
	3.1–130.3	2.2–3.5	G	USSR
Tool and operations: casting				
	0.22–7.5	0.52–4.56	B	Switzerland
	15	12	B	Sweden
	0.7–3.0	0.6–2.6	G	Sweden
	5.5–47.7	1.4–2.1	G	USSR
	21.5	17.6	G	Austria
Tool and operations: forming				
	0.5–24.6	0.97–26.7	B	Switzerland
	0.1–7.5	0.08–5.9	B	Sweden
	0.2–0.7	0.17–0.58	G	Sweden
	–	3.3–32.5	G	USSR
	11.1	8.8	B	Austria
Grinding of sintered pieces: wet grinding without exhaust				
	–	0.2–12.8	B	United States

Source: NIOSH (1977) and references within

B = breathing zone; G = general air

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individuals occupationally exposed were studied in a hard metals plant (NIOSH 1977). Of the 178 hard-metal individuals occupationally exposed (52 men and 126 women), 81% were about 30 years old and about 84% of the individuals occupationally exposed had been engaged in hard-metal operations for 3 years. The concentrations of tungsten in the work atmosphere during various operations varied from 0.75 to 6.1 mg/m<sup>3</sup>. The ranges of mean tungsten concentrations were 0.8–1.1 mg/L in the blood of 45 individuals occupationally exposed and 0.6–1.1 mg/L in the urine of 40 individuals occupationally exposed, while tungsten was not detectable in the blood of 11 individuals occupationally exposed or in the urine of 7. Individuals occupationally exposed in this factory may have been exposed to both soluble and insoluble tungsten compounds. At a factory in Syracuse, New York, which manufactured hard metal parts from tungsten carbide and cobalt, 1 out of 83 cases of individuals occupationally exposed showed appreciable amounts of tungsten carbide concentrations in the lungs (Auchincloss et al. 1992).

Occupational exposure to tungsten and its compounds have also been observed around the world, especially in hard metal industries. In Milan, Italy, individuals occupationally exposed with an average exposure period of 13 years at job functions such as grinding and cutting hard metal materials, had concentrations of tungsten in tissues as follows: lung, 107 ng/g; blood, 1.35 ng/g; and urine, 12 ng/g (Rizzato et al. 1986). A control group of 17 unexposed individuals in this study had concentrations of tungsten in lung tissue, blood, and urine of 1.5, 0.4, and 0.7 ng/g, respectively. In Germany, 87 individuals occupationally exposed in the hard metal manufacturing industry were assessed for exposure to tungsten (Kraus et al. 2001). The median duration of exposure for these individuals occupationally exposed was approximately 13 years. Ambient monitoring yielded a range of tungsten concentrations from 3.3 to 417.0 µg/m<sup>3</sup> in the production of heavy alloys. The highest tungsten concentrations excreted in urine of individuals occupationally exposed were found in grinders (mean, 94.4 µg/g creatinine; maximum, 169 µg/g creatinine). Thus, despite its low solubility, tungsten carbide was bioavailable. Bioavailability of tungsten and its compounds increases in the order of tungsten metal, tungsten carbide, and tungstate ion (Kraus et al. 2001). At two hard metal manufacturing facilities in Sweden, Sahle et al. (1996) reported total dust personal measurements of 1.2±0.7, 1.6±0.8, and 0.8±0.6 mg/m<sup>3</sup> for ammonium paratungstate (APT), blue oxide (WO<sub>2,9</sub>), and tungsten trioxide (WO<sub>3</sub>), respectively. Airborne blue oxide fibers were detected in both static and personal samples when APT was calcined to blue oxide rather than tungsten trioxide.

Occupational exposures have been observed in other industries such as welding shops, smelter/refineries, and shops using tools with cemented tungsten carbide. Brune et al. (1980) determined levels of tungsten in exposed and unexposed individuals from Northern Sweden. Individuals occupationally exposed at a

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smelter and refinery had levels of tungsten which ranged as follows (n=21): kidney, <0.003–0.018 µg/g wet weight; liver, <0.003–0.014 µg/g wet weight; and lung, <0.003–0.15 µg/g wet weight. The range of concentrations of tungsten in tissues from a control group were as follows (n=8): kidney, <0.003–0.005 µg/g wet weight; liver, <0.003–0.036 µg/g wet weight; and lung, and <0.003–0.011 µg/g wet weight. The concentration of tungsten in the workplace air from welding shops in Montréal, Quebec, Canada averaged 0.67 µg/m<sup>3</sup> (n=13; range, <0.15–1.50 µg/m<sup>3</sup>) while the average concentration of tungsten in urban air was 0.0052 µg/m<sup>3</sup> (Haddad and Zikovsky 1985). Lichtenstein et al. (1975) reported the airborne tungsten concentrations in operations involving wet-grinding of tool bits and inserts made of two commercial grades of cemented carbides. The air was sampled with filters in the workers' breathing zones and the filters were analyzed for tungsten. The mean concentration of tungsten was 5.16 mg/m<sup>3</sup> (range, 0.2–12.8 mg/m<sup>3</sup>). Of the 25 samples taken, 40% exceeded 5 mg/m<sup>3</sup>.

Recent toxicological interest in tungsten is based on its increased use as a component of armor-piercing munitions and a replacement for lead in other ammunition. Embedded tungsten shrapnel represents a unique source of internal exposure to tungsten.

Tungsten may be found in human tissues and body fluids. Serum concentrations of tungsten in healthy human subjects are approximately 1–6 µg/L (Bowen 1966; Hartung 1991). The mean tungsten concentrations in the serum of Swedish 15-year-old adolescents from Uppsala and Trollhättan were 0.14±0.2 µg/L (n=355; range, <0.04–1.8 µg/L) for the period between 1993 and 1994 (Bránáy et al. 2002a), while whole blood concentrations for this same population group were <0.2 µg/L (n=326; range, <0.2–0.94 µg/L).

Tungsten occurs in human urine at low concentrations. As part of the National Health and Nutrition Examination Survey (NHANES III) study from 1988 to 1994, 500 urine specimens were analyzed from a nationally representative sample of some 30,000 persons across the contiguous United States and Alaska (Paschal et al. 1998). The mean concentration of tungsten in urine from this study was 1.92 µg/L (n=496; limit of detection=0.3 ng/mL) for all ages and sexes, while the creatinine adjusted mean concentration was 1.92 µg/g creatinine. Between the years of 1999 and 2000, the geometric mean concentration of tungsten in urine for the U.S. population aged 6 years and older was 0.085 µg/L, while the creatinine adjusted mean concentration was 0.079 µg/L (CDC 2003a). Schramel et al. (1997) reported that the mean concentration of tungsten in urine for 14 unexposed individuals was 0.21±0.09 µg/L.

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Tungsten occurs in other body tissues at low concentrations. For example, the concentrations of tungsten in human teeth and mammalian heart tissue were 0.25 and 5 ppb dry weight, respectively (Bowen 1966). For adults, tungsten levels have been determined in human tissues and body fluids: 0.25 ppb in bone; 16 ppb in hair; 2 ppb in heart tissue; <0.7 mg/L in plasma; <0.07 mg/L in serum; 26–160 ppb in skin; 240 ppb in tooth enamel; 2,600 ppb in tooth dentine; and up to 32 µg in urine (Iyengar et al. 1978). Concentrations of tungsten in human teeth, tooth enamel, and tooth dentine vary over a range of 3–6 orders of magnitude. These studies, considered together, provide no basis for explanation of these divergent values.

**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).

Specific information on the exposure of children to tungsten is limited. As for adults in the general population, small exposures occur from normal ingestion of food and inhaling air. These exposures may be higher in areas near industrial facilities that manufacture, processes, recycle, or use tungsten and its compounds.

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

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Tungsten exposure to children from parents' work clothes, skin, hair, tools, or other objects from the workplace is possible if the parent uses tungsten or its compounds at work. However, no cases of home exposure have been reported for tungsten in the literature.

Other home exposures are unlikely since no household products or products used in crafts, hobbies, or cottage industries contain significant amounts of tungsten. One exception is tungsten filaments, which are used in and around the home in light bulbs or other electrical devices.

### 6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Several populations are at high risk for exposure to tungsten and its compounds. Individuals with the highest risk include people who are occupationally exposed to tungsten and its compounds from manufacturing, fabricating, or reclaiming industries (see Section 6.5). In particular, occupational exposures have been reported in industries using hard metals, welding shops, smelters/refineries, and shops using tools with cemented tungsten carbide. Occupationally exposed workers who carry tungsten dust on their clothes from the workplace to their home may increase the risk of tungsten exposure to their family members. People living near tungsten-emitting industries may be at a slightly increased risk of tungsten exposure due to contact with tungsten-contaminated dust within the household, as opposed to ambient air levels.

Populations living in areas with above-average levels of natural tungsten may be at higher risk to exposure. For example, tungsten was found in the municipal water supply of the City of Fallon in Churchill County, Nevada, at a mean concentration of 19.1  $\mu\text{g/L}$  (ppb). In household water derived from private wells in this community a mean tungsten concentration of 37.5  $\mu\text{g/L}$  was obtained (Agency for Toxic Substances and Disease Registry 2003). This was the first finding of excess community-wide exposure to tungsten. At these mean concentrations, the intake of tungsten through drinking water would amount to 38.2 and 75.0  $\mu\text{g}$  per day for residents using water obtained from municipal and private water supplies, respectively, assuming the consumption of 2 liters of water per day. The CDC reported that urine samples of leukemia cases and control subjects from residents in this community had elevated levels of tungsten (CDC 2003b). The mean (geometric) tungsten concentrations in this study was 1.17  $\mu\text{g/L}$  compared with 0.09  $\mu\text{g/L}$  in the U.S. population. However, no correlation was found in this study between incidents of leukemia and elevated levels of tungsten in urine.



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In a follow-up CDC study of Churchill County and three surrounding communities, it was found that the tungsten concentrations in urine followed the concentrations of tungsten in drinking water. The mean (geometric) concentrations of tungsten in the urine of adults in the Churchill County, Yerington, Lovelock and Pahrump communities were determined to be 0.81, 1.04, 0.38 and 0.4 µg/L, respectively, as compared to tungsten concentrations in tap water of 4.66, 3.32, 0.11, and 0.04 µg/L, respectively (CDC 2003c). In children, the mean (geometric) concentrations of tungsten in urine of 2.31, 1.18, 0.62, and 0.56 µg/L were higher than in adults. In addition, the mean tungsten concentrations in urine collected from residents in the Churchill County and three surrounding communities were above the 95% percentile level for tungsten concentrations measured in the general U.S. population.

Patients who have undergone percutaneous coil embolism, which is a medical procedure that is used to occlude unwanted vascular connections such as intracranial aneurysms, aorto-pulmonary, and venous collaterals and coronary artery fistulae, have been found with elevated levels of tungsten in blood and urine (Peuster et al. 2003a). These elevated levels of tungsten are due to the corrosion of tungsten coils that are implanted in blood vessels during the procedure. Tungsten concentrations of <0.7–7.2 and 1.98–837.7 µg/L in blood and urine, respectively, and <10–300 µg/g hair have been reported (Bachthaler et al. 2004). Because of the degradation of the tungsten coils and the elevated tungsten levels found in these patients, coils made from tungsten are no longer used in the percutaneous coil embolism procedure. However, no adverse health effect has been associated with the elevated levels of tungsten within these patients. Military personnel wounded in combat may experience elevated tungsten levels from embedded tungsten-containing ammunition or shrapnel; the toxicological significance of such an exposure scenario has not been determined.

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

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

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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 relevant physical and chemical properties of tungsten and its compounds are available in the literature, but are limited for many tungsten compounds (Ashford 1994; HSDB 2004; Lewis 1997; Lide 2000; O'Neil et al. 2001; Penrice 1997a, 1997b). Additional data on the physical and chemical properties of tungsten compounds would permit estimation of the environmental fate of tungsten and its compounds

**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 2001, became available in May of 2004. This database is updated yearly and should provide a list of industrial production facilities and emissions.

Data regarding the past and present production and import/export volumes for tungsten and its compounds are available (SRI 2003; USGS 2001, 2004a, 2004b). Information about the future production of tungsten and its compounds would be useful. The uses of tungsten and tungsten compounds are well known (ITIA 2001; Lassner and Schubert 1999; Lassner et al. 1996; O'Neil et al. 2001; Penrice 1997a, 1997b; USGS 2002). Tungsten and its compounds are widely used in the home and workplace (O'Neil et al. 2001; Penrice 1997a, 1997b). Limited information on the concentrations of tungsten in food was located in the available literature (Bibak et al. 1998; Perez-Jordan et al. 1998; Rodushkin et al. 1999). Additional information would help to determine whether tungsten may be a contaminant in food. Typical releases of the substance in the home, environment, and workplace indicate that water (Arnórsson and Lindvall 2001; HazDat 2004) and air (Feldmann and Cullen 1997; Fernandez et al. 1992; HazDat 2004; Ondov et al. 1989) are likely to be contaminated with tungsten in areas where natural formations occur or where tungsten is used in industry. Most tungsten minerals, tungsten compounds, and tungsten-containing materials do not require special disposal and handling requirements (see Section 5.4). A significant portion of tungsten is routinely recycled (USGS 2002). Since tungsten and tungsten compounds are not covered under Superfund Amendments and Reauthorization Act (SARA), Title III, manufacturers and users are not required to report releases to the EPA's TRI.

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**Environmental Fate.** Information about how tungsten and its compounds partition in the environment is available (Bidleman 1988; Dermatas et al. 2004; HSDB 2004; Lassner et al. 1996; Meijer et al. 1998; O'Neil et al. 2001; Penrice 1997b; Tanizaki et al. 1992), although it is limited in scope. Additional information about the partitioning of tungsten and its compounds would be useful for determining which environmental media tungsten and its compounds are likely to partition to. The mobility of tungsten has been briefly characterized in soil (Meijer et al. 1998). Additional and comprehensive information about the mobility of tungsten and its compounds would be useful in determining the potential of tungsten and its compounds to migrate into groundwater. Tungsten can change from one chemical form to another, sometimes reversibly, in numerous chemical reactions that can proceed under a wide range of common environmental conditions (Bigham et al. 2001; Bowen 1966; Dermatas et al. 2004; Lassner and Schubert 1999; Lassner et al. 1996; Tanizaki et al. 1992). However, data on the transformation of tungsten and its compounds are limited. Additional information would help to describe the chemical forms of tungsten and its compounds in different environmental media.

**Bioavailability from Environmental Media.** The absorption and distribution of tungsten and tungsten compounds as a result of inhalation or dermal exposures, or oral dosing have been discussed. Limited information on the bioavailability (i.e., adsorption from contaminated air, water, or soil) of tungsten and its compounds is available. Updated and more comprehensive data on the bioavailability of tungsten and its compounds from environmental media are needed.

**Food Chain Bioaccumulation.** Information on the bioconcentration of tungsten and its compounds in plants, aquatic organisms, or animals is not available. Bioconcentration data would be useful in determining the level of storage of tungsten in the organisms as a result of exposure to contaminated media. Information on whether tungsten and its compounds are biomagnified is not available. Biomagnification data would be helpful in determining whether increased levels of tungsten in predators result from consumption of contaminated prey organisms.

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

## 6. POTENTIAL FOR HUMAN EXPOSURE

Information about concentrations of tungsten and tungsten compounds in air (Dames et al. 1970; Haddad and Zikobsky 1985; Jagielak and Mamont-Cieśla 1979; Maenhaut et al. 1979; Sheridan and Zoller 1989), water (Arnórsson and Lindvall 2001; Bowen 1966; CDC 2003b, 2003c; Agency for Toxic Substances and Disease Registry 2003; Hall et al. 1988; Hartung 1991; Johannesson et al. 2000; Kist 1994; Konhauser et al. 1997; Tanizaki et al. 1992a, 1992b; Taylor et al. 1990), soil (Fu and Tabatabai 1988; Penrice 1997a; Quin and Brooks 1972a, 1972b; Senesi et al. 1988), and food (Bibak et al. 1998; Perez-Jordan et al. 1998; Rodushkin et al. 1999) are available, but limited. Updated and more comprehensive data on the concentration levels of tungsten in air, water, soil, and food would be useful to provide a more comprehensive characterization of human exposure. Additional data would also be useful in describing historical trends in tungsten concentrations in various environmental media. Reliable monitoring data for the levels of tungsten in contaminated media at hazardous waste sites are needed so that the information obtained on levels of tungsten in the environment can be used in combination with the known body burden of tungsten to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites. Estimates have not been made for human intake of tungsten and its compounds from various environmental media. These data would help to determine the potential for human exposure to tungsten and its compounds.

**Exposure Levels in Humans.** Tungsten has been detected in the following human tissues and fluids: blood, plasma, and serum (Bowen 1966; Bránáy et al. 2002a; Hartung 1991; Iyengar et al. 1978); urine (CDC 2003a; Iyengar et al. 1978; Paschal et al. 1998; Schramel et al. 1997); teeth (Bowen 1966; Iyengar et al. 1978); heart tissue (Bowen 1966); bone (Iyengar et al. 1978); and hair (Iyengar et al. 1978). Data are also included for tungsten levels in urine from individuals exposed to high (1.82–7.30 µg/L) concentrations of tungsten in drinking water (CDC 2003c).

Although there are data from the CDC study of Churchill County (City of Fallon) and surrounding communities describing the levels of tungsten as in urine of residents exposed to high levels of tungsten in drinking water suggesting that there is no correlation between the high tungsten intake and a cluster of childhood acute lymphocytic and myelocytic leukemias in the Churchill County area (CDC 2003c), leukemias were the only health effect end point examined in the study. It would be useful to know if the tungsten intake measured in CDC study participants is correlated with other health effect end points and populations (e.g., elderly residents) both within this study and in other populations where high tungsten intake has been identified. This information would be useful in assessing the need to conduct health studies on those individuals living near hazardous waste sites or other sites associated with tungsten exposure.

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**Exposures of Children.** Children may be exposed to tungsten and tungsten compounds in the same manner as adults in the general population (e.g., air, food, and water). Exposure and body burden studies on children would be useful. No information was available on unique exposure pathways for children (e.g., pica children, dermal exposure, and parental transport from the workplace). Studies may be needed to determine if unique exposure pathways exist for children, and if they do, to determine the significance they might have on child health. No childhood-specific means to decrease exposure were identified. Child health data needs relating to susceptibility are discussed in 3.12.2 Identification of Data Needs: Children's Susceptibility.

**Exposure Registries.** No exposure registries for tungsten 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.

The population of Churchill County (City of Fallon), Nevada is known to have unusually high exposures to tungsten (CDC 2003b, 2003c; Agency for Toxic Substances and Disease Registry 2003). However, no exposure registry has been established for this population.

### 6.8.2 Ongoing Studies

No ongoing studies investigating potential for human exposure of tungsten or its compounds were identified in the Federal Research in Progress database (FEDRIP 2004).