

A review of tungsten: From environmental obscurity to scrutiny

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Abstract

Since its discovery, tungsten, a transition element of Group VIb of the Periodic Table of Elements, and its compounds have been considered environmentally benign. Its presence in biological and drinking water samples in Fallon, Nevada, an acute lymphocytic leukemia cluster struck community has alarmed public health, environmental and regulatory agencies. Tungsten, a metal of extraordinary properties that make it hardly substitutable, is considered an essential commodity with a wide variety of uses stretching from household necessities to highly specialized applications. This work is undertaken in order to explore aspects of environmental behavior of tungsten and its compounds. Occurrence data in terrestrial, atmospheric, aquatic and biotic systems are presented. Various aspects of environmental chemistry, fate transport across environmental interfaces and toxicology are discussed with the objective of identifying knowledge gaps and outlining directions for future research.

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1. Introduction

Tungsten is a transition metal found, along with chromium, molybdenum and seaborgium, in Group VI of the Periodic Table of elements. Since its discovery in the last quarter of 18th century, tungsten-based products have been in use in a wide range of applications stretching from daily household necessities to highly specialized components of modern science and technology. As new applications and uses are discovered contin-

uously, interest on and demand for tungsten, already an essential commodity, are projected to increase steadily in the years to come. Unavoidably, as is the case with other natural materials and/or non-renewable resources, increased demand and use of tungsten will spawn (a) increased interactions with other materials and/or non-sustainable practices, (b) a greater number of possible entry points into the natural and human environment and (c) a higher probability of deliberate or accidental releases.

Currently, the existing knowledge base does not provide clear information about the behavior of tungsten-based products in the environment. The toxicological profile of tungsten, including possible effects on living organisms and exposure pathways, remains rather sketchy, narrow and fragmentary. Regulation of tungsten, both in terms of environmental and occupational safety and health, is, at present, limited in comparison with other metals. This pattern of environmental obscurity has been unequivocally disrupted by the events of Fallon, Nevada and the possible implication of tungsten to an acute lymphocytic leukemia (ALL) cluster. Tungsten is now the focus of scrutiny as it currently occupies the top of “to do” lists of various regulatory, health and environmental agencies.

This review attempts to: summarize the existing literature on the occurrence, environmental chemistry and toxicology; review the existing regulatory framework in the U.S. and other countries; identify knowledge gaps and outline directions for future

Abbreviations: ACGIH, American Conference of Government Industrial Hygienists; ALL, acute lymphocytic leukemia; BCF, bioconcentration factor; BLM, biotic ligand model; BTF, biotransfer factor for a food product; BSAF, biota/sediment accumulation factor; dimensionless; CDC, Centers of Disease Control; CF, soil-to-plant concentration factor of W; DOM, dissolved organic matter; EEC, effective environmental concentration; EPA, environmental protection agency; EqP, equilibrium partitioning; ITC, interagency testing committee; LD₅₀, lethal dose killing 50% of a group of test organisms; NCEH, National Center for Environmental Health; NIEHS, National Institute of Environmental Health Sciences (Netherlands); NIOSH, National Institute of Occupational Safety and Health; NTP, National Toxicology Program; OSHA, Occupational Safety and Health Administration; PEL, permissible exposure limits; PM_{2.5}, particulate matter of size smaller than 2.5 μm; ppb, parts per billion; ppm, parts per million; STEL, short-term exposure limits; TLV, threshold limit values; TSCA, Toxic Substances Control Act; TWA, time weighted average

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research needs on the environmental relevance of W and W-based products.

2. Background

2.1. Tungsten and leukemia clusters: review of the events

The occurrence of a childhood leukemia cluster in Fallon, Nevada [1] prompted a wide investigation that involved several local, state and federal agencies led by the Centers of Disease Control (CDC) [2–7]. In essence, the objective of this investigation was to assess whether environmental causes were responsible for the cluster. The 16 reported leukemia cases within the time frame of 1997–2001, was well above the average for Nevada (3.0 cases/100,000 children/5 years). Several possible causes were proposed, such as jet fuel (JP-8) from a nearby military base or from a JP-8 pipeline running through the city, high levels of arsenic and other metals in the drinking water supplies, industrial pollution from a local tungsten smelting facility, and agrochemical contamination resulting from agricultural pesticide/fungicide use. Although the exact causes of leukemia are not well-known, genetic and/or environmental factors may trigger the disease including ionizing and electromagnetic radiation, infectious and chemical agents [8].

Extensive testing of drinking water [2], surface water, sediment and biota [3], surface soils and residential indoor dust [4], air [5], as well as cross-sectional exposure assessments of environmental contaminants [6], and the JP-8 fuel pipeline [7] ruled out environmental factors as being responsible for the disease. However, high levels of tungsten were reported in urine (as high as 15 times the national average) [2] and drinking water samples ($0.25\text{--}337\ \mu\text{g l}^{-1}$) [7]. The biological tests also revealed elevated levels of arsenic, seven other metals, and some organophosphate and organochlorine pesticides. None of these contaminants, however, is known to cause leukemia including arsenic, which has been associated with other cancers, but not leukemia.

Soon thereafter, two additional childhood leukemia clusters appeared, one with 12 cases between 1997 and 2003 in Sierra Vista, AZ and the other one with six reported cases in Elk Grove, CA. All locations are rural, desert towns with active or inactive tungsten mines and/or processing operations and military bases near by. High tungsten concentrations were reported in trees from all three communities [9]. Recent tree ring samples consistently showed significant increases in tungsten levels compared to older wood. Trees have been known to translocate metals absorbed through the roots or leaves outward in the trunk thus concentrating them in the younger tissue. As a result of these events, the CDC and the National Center for Environmental Health (NCEH) nominated tungsten for toxicology and carcinogenesis studies [10] and some preliminary findings were published recently [11].

To this date, tungsten has not been the subject of extensive toxicological and/or fate and transport studies and remains one of the least regulated metals. Elevated values in human biological tests, water and tree samples combined with a lack of toxicological information prompted a segment of the scientific community to suspect tungsten as the most “probable cause” for

the leukemia clusters [12]. However, an objective investigation about tungsten sources and mobilization mechanisms is needed, before a “final verdict” can be reached. Here are some questions that need answers. What is the source of tungsten? Is it natural or anthropogenic? How, when and what mechanisms mobilized tungsten? Are anthropogenic activities responsible for this mobilization? Is there evidence from other environmental media (e.g. biota) supporting mobilization?

It is difficult to take sides in a debate on the origin of tungsten in Fallon as ores of that element are indigenous to Nevada’s geologic formations and the area has several (active or inactive) mines and a tungsten smelting plant that operated in the target area for several years [13]. The results of subsequent biological testing in three communities near Fallon [14] also revealed high tungsten values in urine samples, and thus may be supportive of the “natural option” resulting from exposure to elevated values of tungsten in the region’s water supplies.

On the other side of the debate, anthropogenic sources may be in part responsible for contamination of ground and surface water. A tungsten smelting plant in the area operated an open air kiln for over 20 years up to 1994. Atmospheric discharges, prior to 1994 when air pollution controls were installed, could be a possible, but not likely source of soil and water contamination, as prevailing winds place Fallon upwind of the plant [15]. The plant was cited for on/off-site land releases of 240,005 and 100,000 pounds of waste [16,17]. The composition of this waste is not disclosed in the inventory reports, but up to 1990, liquid waste from acid-leaching operations was dumped into the desert. However, the sites of these releases happen to be hydrologically downgradient of Fallon [15].

2.2. Overview of current uses of tungsten

Tungsten has been a relatively little known transition metal despite its remarkable physical and chemical properties including the highest melting point of all elements (except carbon), a boiling point of $5660\ ^\circ\text{C}$, the lowest vapor pressure and expansion coefficient of all metals, very high moduli of compression and elasticity, high density, thermal and electrical conductivity.

Tungsten is considered to be of limited chemical activity and is often cited as non-reactive with strong mineral acids and water. These unique properties, alterable upon demand by alloying with carbon and/or various other metals, make tungsten highly desirable and hardly substitutable in everyday and specialized applications of modern technology. Consequently, tungsten is regarded as an essential commodity and a metal of high strategic importance for years to come [18].

Metalworking, mining and construction industries use tungsten cemented carbides. Tungsten metal wires, electrodes and contacts are used in a wide variety of electrical/electronics applications. Tungsten heavy metal alloys find uses in heat sinks, weights/counterweights, super-alloys for turbine blades, wear-resistant mechanical parts and specialized tools. Chemical uses include catalysts, high-temperature lubricants and inorganic pigments. Widely known civil applications of tungsten include use in incandescent lamp filaments, television sets, magnetrons for microwave ovens and other electrical consumer products, golf

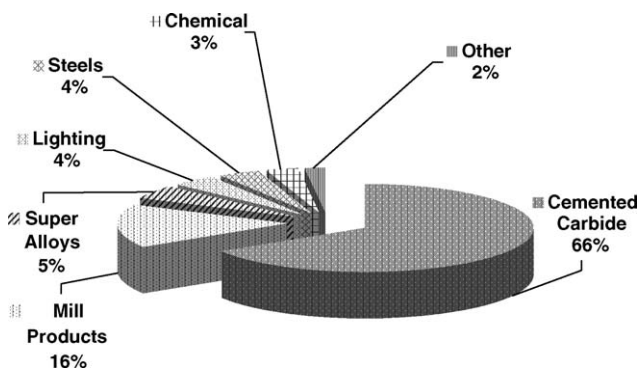


Fig. 1. U.S. tungsten consumption by end use.

clubs, fishing weights and hunting ammunition. Recently, in view of the adverse environmental notoriety of lead and public concerns about depleted uranium, tungsten has been the focus of several military applications including high kinetic energy penetrators, small caliber ammunition and armor plating. The Green Armament Technology (GAT) program, a U.S. Army pollution prevention initiative that calls for substitution of lead by tungsten in small caliber ammunition, has received much publicity. Concerns over adverse environmental effects [19] have also led to the substitution of lead shotshell ammunition and lead fishing weights in various North American and European countries. In the U.S., the Fish and Wildlife Service, approved the use of tungsten–nickel–iron shots as non-toxic for migratory bird hunting effective January 4, 2001 [20].

These initiatives have generated a renewed interest in tungsten and tungsten-based products, which is anticipated to boost to even higher levels an already increasing demand. For the period 1984–1998, U.S. reliance on foreign sources of tungsten materials has increased nearly 40% compared with the average for the previous decade [21]. In 2001, U.S. apparent consumption of all tungsten materials, calculated on the basis of net imports, primary and secondary production, and changes in Government and industry stock levels, was 14,600 metric tonnes, virtually unchanged from that of 14,400 metric tonnes tungsten content in 2000. U.S. tungsten consumption by end use is graphically shown in Fig. 1.

In 2001, world production was at 44,200 metric tonnes tungsten content, approximately 83% of which was contributed by China [21]. The amount of tungsten consumed in products for defense and munitions will increase substantially over the next several years. It is estimated that incremental tungsten consumption based on approved defense related projects, including GAT will range between 2200 and 2700 metric tonnes tungsten content by the year 2006. The GAT program alone would generate an additional demand of 1300–1500 metric tonnes tungsten content per year [22], representing about 10% of the current tungsten demand, ranking third behind cemented carbide and mill product end uses.

2.3. Regulatory status

Much of the revived interest in tungsten and tungsten-based products was based on the premise that tungsten is environmen-

tally “benign”, a notion that seems to permeate through much of the existing environmental regulations and environmental literature.

Exposure limits have been established in the U.S. for soluble and insoluble tungsten compounds in workplace atmospheric environments. Currently, the National Institute for Occupational Safety and Health (NIOSH) permissible exposure limits (PEL), expressed as time weighted average (TWA), stand at 1 and 5 mg m^{-3} of air for soluble and insoluble compounds, respectively. The respective short-term exposure limits (STEL) established by the same agency are 3 and 10 mg m^{-3} of air [23]. The American Conference of Government Industrial Hygienists (ACGIH) has established threshold limit values (TLV) for insoluble tungsten compounds at 5 mg m^{-3} (TWA) and a 10 mg m^{-3} (STEL). Respective values for soluble tungsten compounds stand at 1 mg m^{-3} (TWA) and 3 mg m^{-3} (STEL) [24].

At present, there are no drinking water standards or discharge limits for air, surface water, groundwater or soils in the U.S. The events in Fallon and Sierra Vista alarmed health and regulatory agencies and an interim drinking water threshold level and other tungsten regulations are imminent. Tungsten compounds have been included in the EPA’s toxic release inventory since it was originally published in 1987. However, tungsten has recently been one of thirteen metals included in the CDC National Report on Human Exposure to Environmental Chemicals [25]. In addition to the ongoing toxicology and carcinogenesis study requested by the CDC, and the EPA’s Toxic Substances Control Act (TSCA) Interagency Testing Committee (ITC) recently included 20 tungsten compounds in the Priority Testing List [10].

The Russian Federation regulates tungsten in drinking water (0.05 mg l^{-1}) and fishing lakes and rivers (0.0008 mg l^{-1}) [26,27]. From the above discussion, it is evident that, to this date, tungsten and its compounds remain amongst the least regulated and least studied metal substances.

3. Environmental chemistry and behavior

3.1. Physical and chemical properties of tungsten

Table 1 summarizes the relevant physical and chemical properties of tungsten. A diversity of oxidation states (ranging from -2 to $+6$) and coordination numbers (5–9) make the chemistry of tungsten one of the most varied and complex among the transition elements. Consequently, numerous possibilities exist for formation of soluble complexes with many inorganic and organic ligands (aqua-, oxo-, halide-, organo- and mixed) [32] with implications for enhanced mobility in surface and sub-surface aquatic environments. Unlike tungsten for which some physical and chemical properties are available in the literature, information on many other tungsten compounds is scarce and this is often problematic for an estimation and prediction of the environmental behavior of these compounds.

3.2. Occurrence of tungsten in environmental systems

3.2.1. Terrestrial systems

The earth’s crust, by far the most significant source of tungsten in the ecosphere, is estimated to contain 0.00013% W on

Table 1
Physical and chemical properties of tungsten (compiled from referenced sources)

Property	Value
Atomic number	74
Average atomic mass, g mol ⁻¹	183.85
Atomic volume, cm ³ /mol	9.53
Naturally occurring isotopes, (%)	180 (0.135%); 182 (26.4%); 183 (14.4%); 184 (30.6%); 186 (28.4%)
Pauling electronegativity	2.36
Vanderwaals radius, nm	0.137
Ionic radius, nm	0.068 (+4); 0.067 nm (+6)
Electronic shell	[Xe] 4f ¹⁴ 5d ⁴ 6s ²
Energy of first ionization, kJ mol ⁻¹	768.6
Standard potential, V (W ⁺⁴ /W)	-0.05
Oxidation states	-2, -1, 0, +2, +3, +4, +5, +6
Heat of vaporization [28], kJ mol ⁻¹	824
Heat of fusion [28], kJ mol ⁻¹	35.4
Specific heat [28], J/g K	0.13
Coordination numbers [29]	5, 6, 7, 8, 9
Electrical resistivity [28], μΩ cm	5.5
Thermal conductivity, W/cm K	1.74
Melting point, °C	3410
Boiling point, °C	5660
Vapor pressure [30], Pa (3407 °C)	4.27
Density, g cm ⁻³ at 20 °C	19.3
Appearance [31]	Hard, brittle, steel-gray to tin-white solid

Additional properties may be found in Properties of Tungsten at <http://www.tungsten.com/mtstung.html>.

a mass basis [18], equivalent to an average (background) W concentration of 1.3 mg kg⁻¹. Based on this figure, W occupies the 57th/18th positions in the overall element/metal abundance lists. Surface rocks reportedly contain W at levels in the range of 1.0–1.3 mg kg⁻¹ [33,34]. In terrestrial systems, W exists almost exclusively in the form of oxo-rich tungstate minerals either as *scheelite* (CaWO₄) or *wolframite* ([Fe/Mn]WO₄). Hydrothermal mineralization and metamorphic processes are primarily responsible for the formation of W deposits in subterranean systems and are subsequently transported via high-temperature hydrothermal veins. A more detailed treatment of geochemical/mineralogical aspects of W is provided in Refs. [34–36].

Literature assessing background W concentration levels for soil systems globally is not available and only a limited number of studies exist on a local scale. Studies in the European Union have reported W concentrations in soils (0.5–83 mg kg⁻¹ dry mass) and surface soils (0.68–2.7 mg kg⁻¹ dry mass) [37,38]. The same studies have reported W content levels (in mg kg⁻¹) in the lithosphere (0.1–2.4), phosphate and phosphorite rocks (30–270), limestones and carbonate rocks (0.2–0.8), sewage sludge (1–100), manure (8–2800) and a variety of fertilizers (ND–100). Elevated values in agricultural soils from New Zealand (1.9–21.4 mg kg⁻¹) may be attributed to agrochemical practices [39]. Conversely, values in the range of 0–2 mg kg⁻¹ reported for agricultural soils in Iowa are in close agreement with the background concentration of 1.3 mg kg⁻¹ [40]. High average W concentrations have also been reported for top (56 mg kg⁻¹) and deeper soil (78.4 mg kg⁻¹) formations in the vicinity of mining/smelting sites in North Queensland, Australia [41]. As part of an independent investigation our group detected similar levels

Table 2
Tungsten occurrence in terrestrial systems

Terrestrial system	Concentration (mg kg ⁻¹)	Reference
Earth's crust	1.55	[18]
Lithosphere	0.1–2.4	[36,37]
Surface rocks	1.0–1.3	[33,34]
Surface soils	0.68–2.7	[37,38]
Topsoils (Fallon, NV, USA)	10.0–67.0	This work
Topsoil (near mining/smelting sites, Australia)	56.0	[41]
Fertilized agricultural soils (Europe)	0.5–83	[37]
Agricultural soils (New Zealand)	1.9–21.4	[39]
Agricultural soils (Iowa, USA)	0.0–2.0	[40]
Deeper soil (near mining/smelting sites, Australia)	78.4	[41]
Surface soils (after Gulf War in Saudi Arabian–Kuwait border)	126.5	[42]
Surface soils (300 km away from Saudi Arabian–Kuwait border)	3.25	[42]
Military firing range soils (estimate based on lead)	5200	[43]
Naval firing range soils (estimate for tungsten–tantalum munitions)	5500	[44]
Hunting grounds (estimate)	25.7–58.3	[45]

(10–67 mg kg⁻¹) of W content in topsoils collected from four random locations in Fallon, Nevada within a few miles from radius from an abandoned tungsten mine and a smelting location.

Inflated W contents (126.50 mg kg⁻¹) of surface soils (0–5 cm depth) have been reported in areas close to the Saudi Arabian–Kuwait border as a result of combat operations during the first Gulf War (1990–1991) whereas the W content of surface soils (3.25 mg kg⁻¹) in areas 300 km away from the border remained at levels comparable to natural background concentration [42]. Other sites of military activity with potentially high tungsten concentration are shooting ranges using tungsten-based ammunition. Currently, there are several shooting ranges in the U.S. where tungsten based ammunition has been used on an experimental/developmental basis. Detailed information on firing range site numbers, locations or tungsten soil content levels are not available. However, if the level of tungsten is similar to that of its lead predecessor, then typical concentrations of 5200 mg kg⁻¹ and as high as 200,000 mg kg⁻¹ [43] can be expected. In fact, this typical concentration value is close to an estimate of 5500 mg kg⁻¹ reported by the Air Force Research Laboratory for surface soils in firing ranges where tungsten–tantalum penetrator munitions are used [44]. These values, three orders of magnitude higher than background values in soils, may prove to be of environmental concern. Tungsten recently approved for hunting migratory birds may also pose a concern in civilian firing ranges and hunting grounds. Data are currently scarce, but the Department of the Interior estimates effective environmental concentrations (EEC) of various tungsten-based shots for terrestrial ecosystems in the range of 25.7–58.3 mg kg⁻¹ [45]. Table 2 summarizes occurrence data for W in terrestrial systems.

Natural and anthropogenic transformation and transport mechanisms are responsible for the occurrence of W and its

compounds in the other ecosphere domains (hydrosphere, atmosphere and biosphere). Principal transport and transformation mechanisms of relevance include deposition (wet and dry), advective transport, colloidal transport, chemical precipitation, oxidation/reduction, dissolution, complexation, adsorption and anion exchange. Anthropogenic activities that may contribute to tungsten mobilization include pollution resulting from mining and industrial operations, military combat/training operations using W-containing hardware, agrochemical practices, such as application of W-containing fertilizers, non-sustainable disposal practices of W-containing substances (e.g. disposal of light bulbs in landfills, land application of wastewater residuals) or other substances that could potentially interact with W.

3.2.2. Atmospheric systems

Tungsten, with a vapor pressure of 1 mm Hg at 3000 °C, is the least volatile of all metals. Based on its low vapor pressure and atmospheric interference factor (calculated as the ratio of anthropogenic over natural emissions to the atmosphere multiplied by 100), tungsten is considered to be a lithophilic element (preferring terrestrial over atmospheric or aquatic environments). Sub-nanogram concentrations have been recorded in pristine areas (Arctic/Antarctic) around the globe [46,47]. Tungsten concentrations in ambient air are generally less than 1 ng m^{-3} , but increase moderately in urban, mining/metal processing areas. Air sampling studies over six U.S. cities report atmospheric levels of tungsten in the range of $0.1\text{--}2.0 \text{ } \mu\text{g m}^{-3}$ [48], while other studies performed in urban areas of East Chicago, Indiana and Montreal, Que., Canada have reported values of 6.0 and 5.2 ng m^{-3} , respectively [49,50]. A more systematic study conducted in eight urban areas of Canada reported a mean W concentration of $0.0039 \text{ } \mu\text{g m}^{-3}$ in the particulate fraction ($\text{PM}_{2.5}$) of atmospheric samples [51]. W levels in the plumes of five copper smelting plants in southern Arizona varied from less than 1 to 23 ng m^{-3} [52]. A limited number of studies reported values of tungsten in industrial emission streams. W levels in the range of $5\text{--}21 \text{ } \mu\text{g g}^{-1}$ (ppm) were recorded in fly ash from a municipal waste incinerator in Barcelona, Spain [53]. The W content determined in the smokestack gases of two coal-fired power plants varied in the range of $2.0\text{--}23.2 \text{ } \mu\text{g m}^{-3}$ [54]. The local scale and limited number of these studies cannot provide conclusive evidence that supports atmospheric enrichment resulting from tungsten industrial emissions.

Considering tungsten's lithophilic nature, researchers tend to reason that the limited tungsten enrichment observed on a global and regional scale, relative to its natural abundance on the Earth crust, is not of anthropogenic origin. However, recent studies indicate that tungsten can be transformed via multiple reactions to soluble or even volatile species. Evidence of the latter is presented in a study on the occurrence of volatile transition metal compounds in three municipal waste landfills. Tungsten hexacarbonyl ($\text{W}(\text{CO})_6$) was measured at concentrations in the range of $0.005\text{--}0.01 \text{ } \mu\text{g}$ of W per m^3 of gas [55]. It is claimed that reactions of metallic tungsten with carbon monoxide produced by anaerobic reactions within a landfill environment could be the source. Since metallic tungsten is widely used in common household products, such as light bulbs, its presence in detectable

amounts in municipal solid waste as well as in landfill leachates is not surprising, even though specific studies have not been conducted. The toxicological behavior of tungsten hexacarbonyl is not known. However, according to the authors a comparison with nickel tetracarbonyl [$\text{Ni}(\text{CO})_4$] is inevitable given the proximity of the two metals on the periodic table of elements [55]. In view of the fact that exposure to nickel tetracarbonyl is regulated, and in certain countries it is even considered a carcinogen, concerns about a possible similar behavior of tungsten hexacarbonyl cannot be readily discounted.

Other tungsten compounds of relevance for atmospheric environments include tungsten carbide (WC), tungsten hexachloride (WCl_6), tungsten hexafluoride (WF_6) and tungsten oxide fibers (WO_x). Although vapor pressure or other solid/liquid–gas partitioning data for most of these compounds are not generally available, aerosols and particulates are assumed to be the relevant W-compound bearing fractions in gaseous streams. Certain W-compounds, however, can exist in the vapor phase either because of volatility (e.g. tungsten carbonyl has a vapor pressure of 0.1 mm Hg at 20 °C), or because they are gases under normal conditions (e.g. tungsten hexafluoride is a gas at room temperature). Ample literature implicates several of these compounds in *interstitial pulmonary fibrosis* (“hard metal disease”). Much of this literature originates from workplace environments in several countries around the globe with tungsten-rich deposits and/or sites of intense related mining/industrial activities and is reviewed in references [9,24,56,57]. Concentrations close to 8.0 mg m^{-3} in atmospheric workplace environments have been reported [56]. W-oxides (WO_x) have attracted considerable attention as fibers of these materials, greater than $0.5 \text{ } \mu\text{m}$ size, may be generated in high numbers ($>38.3 \text{ fibers ml}^{-1}$) in dusty workplace environments during various W-production stages [56]. Although the exact role of W-oxides in lung fibrosis is still debated [58], W-oxides are currently under toxicological and carcinogenicity scrutiny [59]. Additional concerns involving occurrence, fate and transport of W-oxides in atmospheric environments may arise as a result of novel applications, e.g. conductance type gas sensors [60], photochemical aerosol generators [61,62], particle accelerators [63] and nanomaterials [64] of W-oxides (particularly WO_3) as a result of their unique electro-optical, electrochromic, ferroelectric, catalytic properties, electrical conductivity and adsorption properties. A summary of occurrence data for W in atmospheric systems is given on Table 3.

3.2.3. Aquatic systems

W can be released to aquatic systems via multiple natural or anthropogenic routes from terrestrial, atmospheric and biotic environments. A non-exhaustive list of natural processes includes weathering of W-rich rocks and soils, dissolution, hydrothermal and volcanic activity, atmospheric precipitation (wet and dry) and excretion of metabolites. Anthropogenic sources include a variety of industrial, commercial and military activities along with non-sustainable disposal practices of municipal, agricultural and industrial wastes. Unlike the atmosphere where particulate forms are dominant, both soluble and particulate W forms can exist in aquatic environments,

Table 3
Tungsten occurrence in atmospheric systems

Atmospheric system	Concentration (ng m ⁻³ unless otherwise noted)	Reference
Air (pristine areas Arctic/Antarctic)	<1.0	[46,47]
Air (6 major cities in USA)	0.1–2.0 μg/m ³	[48]
Air (PM _{2.5} from 8 urban areas Canada)	3.9	[51]
Urban area air (East Chicago, IN, USA)	6.0	[49]
Urban area air (Montreal, Canada)	5.2	[50]
Smelting plant emissions (AZ, USA)	1–23	[52]
Fly ash (incinerator Barcelona, Spain)	5–21 mg kg ⁻¹	[53]
Smokestack gases (coal-fired power plant)	2.0–23.2 μg m ⁻³	[54]
Landfill gas ((W(CO) ₆ reported as W)	0.005–0.01 μg m ⁻³	[55]
Atmospheric workplace (W smelting facility)	8.0 mg m ⁻³	[56]

the former being of higher environmental concern because of higher mobility and toxicity. W exists naturally in ocean water and sediments, surface water bodies and groundwater in areas of hydrothermal activity while anthropogenic emissions and transport from other systems are responsible for W presence in other aquatic systems.

W is present in oceanic waters in trace amounts generally at levels below 1 ng kg⁻¹ [65], whereas a typical value of 0.2 ng kg⁻¹ is most often cited [66]. W content for Northern Atlantic and Pacific Oceans reported in the literature are 100 and 8 ng l⁻¹, respectively [67]. Due to the lack of other verifiable data, the elevated value for the Northern Atlantic Ocean cannot be attributed with certainty to enrichment reflecting the intensive industrial activity known to exist in this region of the globe. Although data are not readily available, deep hydrothermal vents and marine sediments are known environments of increased tungsten availability. Data were recently published for hydrothermal vent fluids in three known locations in the Indian Ocean (0.039 μg kg⁻¹), North Pacific Ocean (2.8 μg kg⁻¹) and East China Sea (22.6 μg kg⁻¹). The latter represents an increase of four orders of magnitude over the background seawater level [68]. Similar high values for marine sediments (10–60 μg kg⁻¹) are reported in literature cited by Ref. [69].

Surface and groundwater in areas of tungsten deposition, or hydrothermal activity as well as in alkaline lakes in arid regions are also known to contain elevated values of W. Values as high as 70 mg kg⁻¹ have been reported for concentrated brines of Searles Lake, CA [70]. Samples analyzed at multiple points along the reach of three river systems (Truckee, Walker and Carson) in Nevada showed W levels in the ranges of 0.319–72.1, 0.15–4.07 and 1.51–189.7 μg l⁻¹, respectively [71]. A systematic analysis of groundwater from an aquifer, located downgradient from the potential nuclear waste repository at Yuca Mountain, Nevada, generated results that varied in the range of 0.10–4.36 μg kg⁻¹ [72]. Studies on Nahanni River water, hot springs and groundwater in scheelite/wolframite bearing areas of the Northwest Territories of Canada showed W concentrations as high as 224.5 μg l⁻¹ [73]. Values in the range of 0.005–11.5 μg l⁻¹ were reported in glacial and thermal waters in areas known to bear formations of natural W minerals in Northern Iceland [74].

Tungsten enrichment in surface and groundwater resources resulting from anthropogenic activities is evident in the limited number of studies available in the literature. Average W concentrations of 0.05, 0.15 and 0.08 μg l⁻¹ have been reported for the waters of three rivers (Mahanadi, Brahmani and Baitarani) flowing through industrial areas of the Indian peninsula [75]. Data have been presented for two rivers in Japan, Tamagawa and Sagami, the former flowing through a primarily industrial basin discharging in Tokyo Bay and the latter flowing through an agricultural basin discharging in Sagami Bay. The W load of the Tamagawa River (industrial area) is distributed approximately equally in the particulate (0.006–0.104 μg l⁻¹) and dissolved (0.038–0.107 μg l⁻¹) fractions and is generally enriched along the reach of the river. For the Sagami River (agricultural area), the W content is mostly distributed in the dissolved fraction (0.027–0.028 μg l⁻¹) with small amounts present in the particulate (0.003–0.004 μg l⁻¹) fraction and is virtually constant throughout its reach. The authors of Ref. [76] suggest that W can exist in oxy-anionic soluble forms (primarily WO₄²⁻), but also as species associated with the small inorganic colloids. Similar values have been reported by the same group of researchers for three other rivers in Japan [77]. Very high W enrichment has been documented in the sediment of a reservoir in a mining area of Germany (near Dresden). W levels of 52 mg kg⁻¹ reflect an enrichment factor of 9 within a period 81 years [78]. W detected in trace amounts in the particulate (0.14 ng l⁻¹) and dissolved (0.76 ng l⁻¹) fractions of rainwater nearby a hard-metal industrial plant in Russia was attributed to atmospheric emissions from that plant [79]. W was found in roadside soils (7.40–63.9 mg kg⁻¹) [80] and runoff (<25 mg l⁻¹) [81,82] at high concentrations possibly indicating an impact from studied tires. Sequential extraction data provided in these studies show that W is roughly distributed equally in the residual (48.0%) and oxidizable fractions (47.6%) with minor amounts present in the reducible (3.3%) and acid/exchangeable (1.1%) fractions.

The presence of W and its compounds is not considered likely for the majority of public drinking water supplies in the U.S. and other economically advanced countries. However, in the absence of any kind of regulation in aquatic environments, W is not part of routine testing programs. With the exception of some Russian studies [83–85] that probably served as the basis of W regulation in aquatic systems for that country, literature specifically dealing with occurrence of W in drinking water supplies is rather limited. A French study performed in groundwater, used as production source for bottled mineral water, in several sites in Vichy reported an average tungsten content of 62.73 μg l⁻¹ (range: 0.4–112 μg l⁻¹) with no statistically significant difference between W levels in groundwater and bottled water [86]. The events in Fallon, Nevada prompted several investigations of the town's drinking water supply. W was detected in all 77 tap water samples in concentrations ranging from 0.25 to 337 μg l⁻¹ with an average concentration of 19.9 μg l⁻¹ [87]. The highest W levels were detected in households using private wells. As part of our independent testing conducted at six random sites in the town of Fallon in the summer of 2003,

Table 4
Tungsten occurrence in aquatic systems

Aquatic system	Concentration (ng kg ⁻¹ unless otherwise noted)	Reference
Ocean water	1	[65]
Ocean water (typical)	0.2	[66]
Northern Atlantic Ocean	100	[67]
Pacific Ocean	8	[67]
Hydrothermal vent fluids (Indian Ocean)	39	[68]
Hydrothermal vent fluids (North Pacific Ocean)	2800	[68]
Hydrothermal vent fluids (East China Sea)	22600	[68]
Marine sediment	10–60 mg kg ⁻¹	[69]
Concentrated brines (Searles Lake, CA, USA)	70 mg kg ⁻¹	[70]
Truckee River water (NV, USA)	0.319–72.1 µg l ⁻¹	[71]
Walker River water (NV, USA)	0.15–4.07 µg l ⁻¹	[71]
Carson River water (NV, USA)	1.51–189.7 µg l ⁻¹	[71]
Nahanni River (river, hot springs, groundwater Northwest Territories, Canada)	224.5 µg l ⁻¹	[73]
Carson River water	1.5–23 µg l ⁻¹	[72]
Groundwater (aquifer downgradient of Yuca mountain, NV, USA)	4.36 µg l ⁻¹	[72]
Glacial and thermal waters (Northern Iceland)	0.005–11.5 µg l ⁻¹	[74]
Mahanadi River (India)	0.05 µg l ⁻¹	[75]
Brahmani River (India)	0.15 µg l ⁻¹	[75]
Baitarani River (India)	0.08 µg l ⁻¹	[75]
Tamagawa River (industrial area, Japan)		
Particulate fraction	0.006–0.104 µg l ⁻¹	[76]
Dissolved fraction	0.038–0.107 µg l ⁻¹	[76]
Sagamigawa River (agricultural area, Japan)		
Particulate fraction	0.003–0.004 µg l ⁻¹	[76]
Dissolved fraction	0.027–0.028 µg l ⁻¹	[76]
Sediment in reservoir (mining area, Dresden, Germany)	52 mg kg ⁻¹	[78]
Rainwater (hard-metal plant, Russia)		
Particulate fraction	0.14 ng l ⁻¹	[79]
Dissolved fraction	0.76 ng l ⁻¹	[79]
Drinking water (Vichy, France)	0.4–112 µg l ⁻¹	[86]
Tap water (Fallon, NV)	0.25–337 mg l ⁻¹	[87]
Tap water (Fallon, NV)	64–135 mg l ⁻¹	This work
Drinking water wells	0.27–742 µg l ⁻¹	[19]

W was detected in samples in concentrations varying in the range of 64–135 µg l⁻¹. A follow-up study has recently published results of extensive testing of 100 drinking water wells from all aquifers in the Fallon area, where W concentration ranged from 0.27 to 742 µg l⁻¹ [15]. This study suggested that the source of W in the study area is natural and identified four major contributing mechanisms, namely (a) evaporative concentration in river water, (b) intermixing with geothermal waters, (c) dissolution/precipitation of W minerals in sediments and (d) adsorption/reductive dissolution of W in Fe and Mn oxyhydroxides. Occurrence data for W in aquatic systems are summarized in Table 4.

Table 5
Tungsten occurrence in plant systems

Plant system	Concentration (mg kg ⁻¹ unless otherwise noted)	Reference
Trees and shrubs (Rocky Mountains)	5–100	[91]
Eucalyptus (North Queensland, Australia)		
Leaves	13.6	[41]
Young stems	2.9	[41]
Old stems	4.3	[41]
European beech tree leaves	7–50	[93]
Oak tree bark (Czech Republic)	0.129–4.79	[94]
Onions (Denmark)	6.3–39 µg kg ⁻¹	[95]
Berries (Sweden)	0.22–7.2	[96]
Cabbage	0.2–1.7	[97]

3.2.4. Biotic systems

W can be transported to biotic systems from terrestrial, atmospheric or aquatic systems via several mechanisms including uptake by plants, trees and vegetative matter, bioaccumulation in microbial and animal organisms, sorption/desorption, formation of organotungsten compounds and subsequent partitioning in organic matter, and excess metal sequestration.

The role of tungsten in biological systems has been established only recently. For years there existed a notion that this element, a close relative of molybdenum whose role in molybdoenzymes is well established, has a functional role in living matter. Mixed indications that the presence of W may cause growth enhancement or moderate toxicity to certain microbial, plant, and animal species have been reported in Refs. [88,89]. A thorough review on tungsten in biological systems with numerous references, covering microorganisms, plants and animals, has been published fairly recently [68]. In this section, only a summary and selected works published in the last 10 years pertaining to the occurrence of W in plants are presented. For a discussion of the occurrence of W in other constituents of the biotic environment, the reader is directed to the toxicology section of this review. A summary of occurrence data in various plants is provided in Table 5.

Plants are known to take up (possibly in anionic form, WO₄²⁻ [90]) and accumulate tungsten in substantial amounts. The extent of accumulation appears to be directly related to the W content of the soil irrespective of the source nature (natural or anthropogenic) and varies widely depending on the plant genotype. Certain plants (e.g. tomatoes) act as excluders of W, particularly in the presence of Mo [68]. Concentrations of 5–100 mg kg⁻¹ were found in trees and shrubs in the Rocky Mountains [91], whereas values below 1 mg kg⁻¹ appear to be most common in other plant types [92]. Elevated values of W have been reported in the leaves (13.6 mg kg⁻¹), young stems (2.9 mg kg⁻¹) and old stems (4.3 mg kg⁻¹) of eucalyptus trees (*Eucalyptus melanophloia*) in the vicinity of an inactive wolframite mine in North Queensland, Australia compared to control values of 0.1, 0.0 and 0.1 mg kg⁻¹, respectively [41]. W detected in the leaves of European beech trees (*Fagus sylvatica*) varied in the range of 7–50 mg kg⁻¹ and was attributed primarily to atmospheric

deposition [93]. A Czech study reported a mean W concentration of 0.775 mg kg^{-1} in oak tree bark (range $0.129\text{--}4.79 \text{ mg kg}^{-1}$) [94]. Information has been presented earlier on elevated values of W in tree ring samples taken from Fallon, Nevada and other ALL struck communities [9]. Limited literature exists on food crops. W was detected in onions harvested in various sites (Denmark) at a mean level of $16.7 \mu\text{g kg}^{-1}$ fresh mass ($n = 64$; range, $6.3\text{--}39 \mu\text{g kg}^{-1}$) [95], in two wild berry species in Sweden at levels in the range of $0.22\text{--}7.2 \text{ mg kg}^{-1}$ [96] and in cabbage ($0.2\text{--}1.7 \text{ mg kg}^{-1}$) grown in fly ash-amended soils [97].

Although certain plants are capable of acting as W accumulators or excluders, plant toxicity has also been reported in the literature. Accumulation and toxicity of W on rye grass was reported recently [98]. The accumulation increased as the W soil concentration increased from 0.1 to $10,000 \text{ mg kg}^{-1}$. At the highest soil content level, toxicity became apparent throughout the life of the plant and resulted in death, approximately 4 weeks after germination. Accumulation of W, investigated using three species of *Brassica* (fast plants, red cabbage and Indian mustard), was attributed to anthocyanins [99]. The same study concluded that replacement of Mo in nitrate reductase by W is a likely toxicity mechanism and that sequestration of excess metals in the peripheral cell layers appears to be a common mechanism of plant metal accumulation. Sequestration of metals in tissues where these substances are less harmful to the plant, or plant defense against pathogens or herbivores are two plausible explanations.

3.3. Environmental chemistry of tungsten

Tungsten, with oxidation states ranging from -2 to 6 and coordination numbers from 5 to 9 , is capable of forming a large number of soluble complexes with a variety of inorganic and organic ligands [32,100]. For instance, tungsten(V) gives the octahedral halogen complexes WX_6^- ($X = \text{F}, \text{Cl}$ and Br) and also WF_8^{3-} . For oxidation state III, tungsten forms face-sharing bioctahedral species of the form WX_9^{3-} in which strong $\text{W} \equiv \text{W}$ triple bonds are formed. Numerous mixed ligand complexes of the type $[\text{WX}_n\text{L}_{6-n}]$ ($\text{L} =$ ligand molecule other than halogen) are also formed. Aqua and oxo complexes of tungsten are of special interest for assessing its subsurface mobility. From the $\text{W}_3\text{O}_4^{4-}$ aqua ion many complexes can be obtained by replacing some or all of the nine outer water molecules by other ligands. Examples are the $[\text{W}_3\text{O}_4\text{F}_9]^{5-}$ and $[\text{W}_3\text{O}_4\text{L}_3]^{4+}$, where L is an organic ligand. Tungsten(VI) forms a few oxo complexes, such as $[\text{WOF}_5^-]$, $[\text{WO}_2\text{F}_4^{2-}]$, $[\text{WO}_2\text{Cl}_4^{2-}]$ and $[\text{WO}_3\text{F}_3^{3-}]$ [32].

The reactions of W with water play a major role in the behavior and mobility of this element and its compounds in the environment. Potential-pH equilibrium diagrams and pertinent reactions of W-water systems, under conditions of thermodynamic equilibrium at 25°C , in the absence of complexing/precipitating substances, taking into account the WO_4^{2-} and the solid substances W, WO_2 , W_2O_5 and anhydrous WO_3 , have been generated by Pourbaix [100]. Although these constraints limit seriously pragmatic inferences to natural systems, the diagrams clearly indicate the complexity of the chemical behavior of tungsten in aqueous solutions even in the absence

of complexing/precipitating agents, alloyed metallic elements or interfaces (e.g. soil particles). W, a base metal with a domain of stability below that of water, under alkaline conditions has a tendency to dissolve WO_4^{2-} while forming non-protective oxide layers. According to Lassner and Schubert [32], the reaction of metallic tungsten with distilled water is very slow at low temperature (38°C), corresponding to a corrosion rate of $3.8 \mu\text{g m}^{-2} \text{ h}^{-1}$ and resulting in an equilibrium tungstate concentration in solution of 10^{-3} M (equivalent to 184 mg l^{-1} of W). The environmental behavior of tungsten once it dissolves becomes very complex as the tungstate anion occurs monomerically only in alkaline or neutral solutions. Under even slightly acidic conditions tungstates tend to polymerize to form isopolytungstates with possible biotic toxicity implications [101,102].

The ability to polymerize is common for elements in Groups V and VI of the Periodic Table. The monomeric state of tungstate is only stable at $\text{pH} \geq 6.2$ in solutions free of complexing agents. A simplified scheme of the tungstate polymerization process along with relevant pH and time scales is shown in Fig. 2 [103].

Speciation can also be described in terms of pC–pH diagrams. However, databases for tungsten species are not readily available as most of these species are difficult to be determined analytically. The speciation diagram shown in Fig. 3 was produced using VISUAL MINTEQ Version 2.3. Table 6 lists the species considered along with their respective equilibrium constants. The runs were based on a 0.005 M total concentration of sodium tungstate in a 0.01 M solution of NaCl allowing solid species (such as tungstic acid) to precipitate. Smith and Patrick [104] studied the speciation equilibrium of sodium metatungstate ($\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}]$) in the pH range 4.5 to 10 using NMR spectroscopy. Sodium metatungstate was found to decompose with the addition of a base to paratungstate A ($\text{W}_7\text{O}_{24}^{-6}$), which slowly converted to paratungstate B ($\text{H}_2\text{W}_{12}\text{O}_{43}^{-10}$). Equilibration may take up to 8 months to be achieved and the major stable polytungstates species are the monomeric WO_4^{2-} , $\text{W}_7\text{O}_{24}^{-6}$, $\text{H}_2\text{W}_{12}\text{O}_{42}^{-10}$ (solid phase) and $\text{H}_2\text{W}_{12}\text{O}_{40}^{-6}$. The environmental implications of these transformations are not addressed. However, from the available literature and modeling studies, it appears that tungstate is the principal soluble species in alkaline environments, whereas a number of possibilities for polymerized forms prevail at acidic environments. The situation is infinitely complicated in the presence of redox, complexing and precipitating agents, interfaces and organic compounds.

Short-term dissolution of W and WO_3 in distilled water has recently been reported. WO_3 equilibrium in distilled water, attained within 48–72 h, results in concentrations of about $500 \mu\text{g l}^{-1}$ W in the aquatic phase, while metallic W, after 9 days of equilibration, still dissolves at a rate of $500 \mu\text{g day}^{-1}$ [105,106]. In both cases the dissolution process is accompanied by a significant pH drop and dissolved oxygen depletion. The effect of the presence of alloying elements (Co, Fe and Ni) on W dissolution was also reported in long-term dissolution experiments [106]. Dissolved oxygen depletion accompanies the dissolution process regardless of alloy composition and initial pH, whereas a pH drop is observed, when the initial pH is alkaline or neutral, but reverses direction for acidic initial pHs. Although a detailed mechanism for W dissolution is not

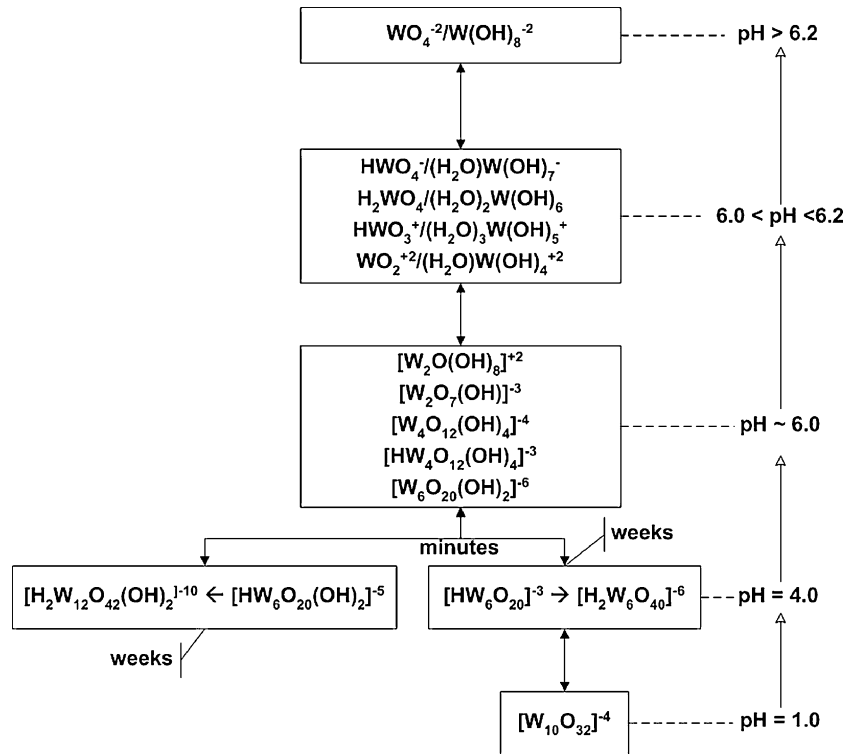
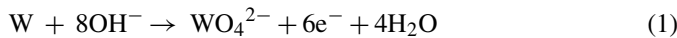


Fig. 2. Tungsten speciation as a function of pH (based on Refs. [32,103]).

elucidated in [106], it is suggested that anodic oxidation of metallic tungsten accompanied by cathodic reduction of dissolved molecular oxygen take place according to the following simplified half-reaction scheme:



The dissolution behavior of W can be of high environmental relevance in natural ecosystems as hypoxia and acidification are two conditions with significant implications for speciation, reactivity, mobility and toxicity of tungsten or other stressors.

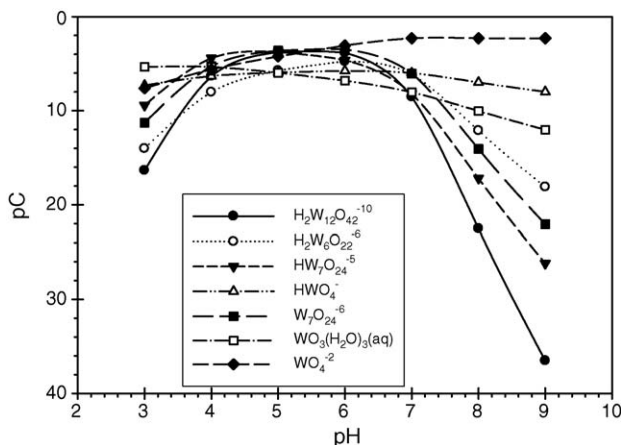


Fig. 3. pC–pH diagram for a solution of sodium tungstate 0.005 M in 0.01 M NaCl (VISUAL MINTEQ Version 2.3).

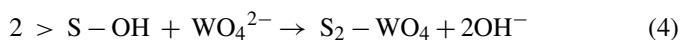
Upon dissolution, depending on prevailing conditions (temperature, pressure and pH), presence of other ions, and/or complexing agents, several possibilities exist for transformation. Formation of insoluble or sparingly soluble tungstates, possibly accompanied by reprecipitation/coprecipitation, are known to form in aquatic environments in the presence of salts of divalent and trivalent metals (except Mg). Alkali tungstates are highly mobile in aquatic media as they are very soluble in water. Under acidic pH, the formation of a number of isopolytungstates is possible, but their stability and optimal H_3O^+/WO_4^{2-} ratio is influenced by the presence of other anions. For example, the presence of ammonium may shift polycondensation to higher pH values. Competition of tungstate species with other anionic species is also of high environmental relevance with implications for particulate and colloidal transport as a result of sorption and/or ion exchange.

Although the lithophilic nature of W and its compounds is undisputable little information exists in the literature on adsorption/desorption behavior [107,108]. Over the last 2 years, our group has performed several experimental studies to determine

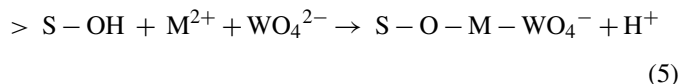
Table 6
VISUAL MINTEQ tungsten species and equilibrium constants

Reaction	Equilibrium constant, pK
$12WO_4^{2-} + 14H^+ \rightleftharpoons H_2W_{12}O_{42}^{10-} + 6H_2O$	111.5
$6WO_4^{2-} + 6H^+ \rightleftharpoons H_2W_6O_{22}^{6-} + 2H_2O$	48.4
$7WO_4^{2-} + 9H^+ \rightleftharpoons HW_7O_{24}^{5-} + 4H_2O$	71.24
$WO_4^{2-} + H^+ \rightleftharpoons HWO_4^-$	3.62
$WO_4^{2-} + 8H^+ \rightleftharpoons W_7O_{24}^{6-} + 4H_2O$	65.19
$WO_4^{2-} + 2H^+ \rightleftharpoons WO_3(H_2O)_{aq}$	8.7

adsorption and leaching behavior of dissolved W species on model natural soils and nanocrystalline (crystal sizes 3–7 nm) titanium dioxide hydrate [105,106]. A better understanding of the environmental behavior of W and identification of possible remedial schemes for W-contaminated environmental matrices were the basic objectives of these studies. Adsorption/desorption experiments, carried out using solutions resulting from dissolution of powders containing alloying elements in proportions found in certain munitions formulations (Ni/Fe, Ni/Co and Ni/Co/Fe), using four model soils (montmorillonite, illite, sigma sand and Pahokee peat) have been described in Ref. [106]. The adsorption behavior was described adequately by Freundlich isotherms while hysteretic desorptive behavior was evident in all cases. Although a significant uptake was observed in all model soils, the amount of dissolved W species adsorbed by Pahokee peat (containing about 90% organic) was by far the highest. This preference of dissolved W species for the organic phase may be an indication of possible interactions with the organic matter present on that particular soil. The adsorption behavior of W on the inorganic soils also accompanied by a simultaneous pH increase can be attributed to chemisorption of the tungstate anion on a reactive metal hydroxyl sites according to the reactions:



or to formation of ternary complexes according to the following reaction:



The presence of phosphates in solutions containing dissolved W species affects the sorption behavior of the latter and acts as a competitor for adsorption sites. This behavior was evident in a series of experimental runs carried out to explore remedial treatment of aquatic solutions containing dissolved W species by adsorption on nanocrystalline (crystal sizes 3–7 nm) titanium dioxide hydrate. Solutions containing variable combinations and amounts of dissolved W, Cu, Fe, Ni and P (as PO_4^{3-}) were passed through a column containing the Ti-based adsorbent mixed with sand to produce a desirable porosity bed. Results plotted in Fig. 4 are for a leaching solution resulting from dissolution of a powder consisting of W, Cu with or without addition of phosphates. The presence of phosphate anions resulted in an early breakthrough of tungsten (after 800 ml) compared with the solutions without phosphate amendment (1200 ml). Normalized concentration values (C/C_0) for phosphate amended solutions reached values larger than unity suggesting phosphate displacement of sorbed tungsten. The same behavior was observed for all the other solutions used in our experiments. Additional experiments were subsequently designed and performed using three model soils in order to confirm that this competitive behavior is not due to some peculiarity of the TiO_2 adsorbent. The results, shown in Fig. 5, indicate a significant decrease in the adsorptive capacity for Pahokee peat soil, but not for montmorillonite and illite soils, where the adsorptive capacity remains unaf-

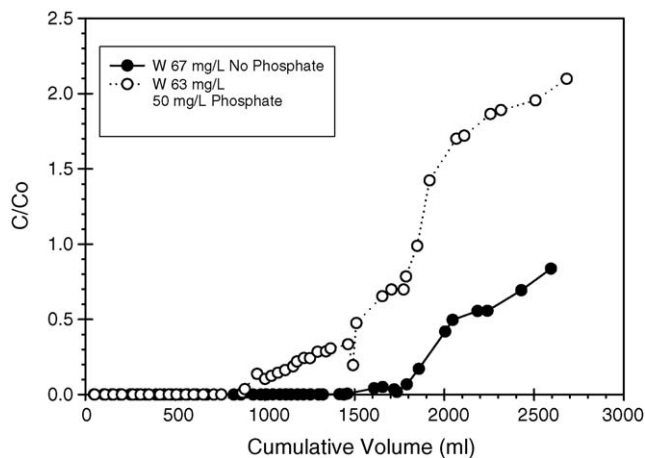


Fig. 4. Tungsten breakthrough curve for W/Cu solution with and without phosphate.

ected or slightly improves. Nevertheless, competitive adsorption between certain anionic species and dissolved W forms may be of significance in natural environmental systems as this may serve as a mobilization mechanism for W and is certainly an area where more research is needed.

The presence of organic matter may induce two major types of interactions with metals in environmental systems: (a) by influencing metal partitioning between various environmental compartments and interfaces and (b) by means of biochemical reactivity resulting in the formation of organometallic substances. The presence of dissolved organic matter (DOM) was shown to affect the distribution bioavailability of other metals (e.g. Ag and Cd [109]) but relevant studies on tungsten have not been published. The presence of DOM, specifically the dissolved fulvic and humic acid fraction, may affect a metal's toxicity not only by acting as a complexing agent in solution, but also by interacting directly at the biological interface as a natural surfactant or directly competing with W for anion exchange sites. No studies have been reported in the literature on interactions between W and DOM.

W and the other transition metals (Cr and Mo) with their diverse array of chemistry are very popular for synthetic

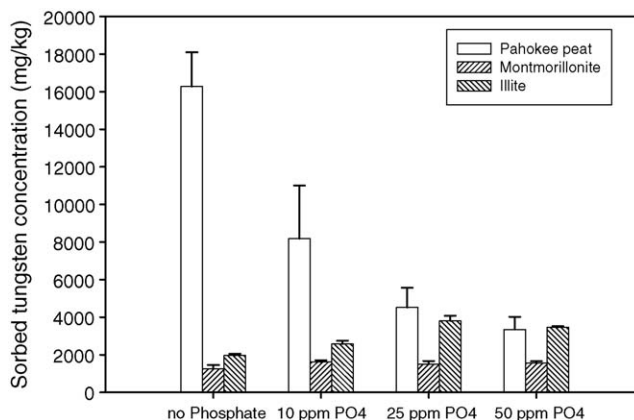


Fig. 5. Uptake of tungsten by model soils in the presence of different concentrations of phosphate. Error bars represent the standard deviation of 3/4 replicates.

methodology development of organometallic compounds [110] with a wide variety of applications extending from catalysis to semi-conductors and optochemical environmental sensors. Concerns exist not only for organotungsten compounds introduced to the environment in the form of synthesized compounds, but also for compounds formed endemically in the natural environment (soil, sediment, water and air) as a result of biochemical interactions of natural or anthropogenic tungsten with organic compounds or ligands. The former are easier to control by regulation, green design, pollution prevention, treatment and combinatorial measures. The formation and ultimate fate of the latter is nearly impossible to predict, as they are subject to the stochastic nature of natural phenomena, pollution history related uncertainties and spatial/temporal and other constraints. During the last decade, environmental literature of organometallic compounds, though still limited, has been rapidly expanding [110–112]. However, literature on the formation and environmental behavior of W-organometallic substances in natural systems is non-existent, although certain organotungsten compounds have been detected in natural environments. Tungsten hexacarbonyl, $W(CO)_6$ formation and occurrence in municipal landfill gases has been presented earlier. $W(CO)_6$ is a white crystalline solid (density 2.65 g cm^{-3}) with a low vapor pressure (13.3 Pa at 20°C and 160 Pa at 67°C) [32]. Its formation was theorized to take place as a result of direct action of carbon monoxide present in anaerobic landfill environments on tungsten, possibly originating from light bulb filaments or other solid waste sources. [55]. A common transformation mechanism referred to as biomethylation is known to be mediated by natural anaerobic microbial organisms resulting in the formation of methyl-metal compounds $(CH_3)_xM$ (M =metal). However, methylated tungsten compounds (e.g. hexamethyltungsten, $W(CH_3)_6$) although synthetically possible [113,114] and stable [115], are essentially unknown in nature.

3.4. Fate and transport of W

The distribution and fate of tungsten in the environment is governed partly by its physical, chemical and biological properties and partly by the prevailing environmental conditions. As a metal, W is infinitely persistent, but can exist in various interchangeable forms often across different environmental compartments via chemical speciation, reactivity or mobility. Environmental exposures of humans and ecosystems include release of W by natural processes (e.g. volcanic/hydrothermal activity, erosion and bioaccumulation) and anthropogenic processes (e.g. mining, smelting, industrial/commercial activities and waste disposal practices). Since the earth's crust is the pool

of W in the ecosphere, it is a good starting point for considering the environmental cycling of W.

The distribution of W between soil and water is expressed by the soil–water partition coefficient, K_d defined as:

$$K_d = \frac{C_s}{C_w} \quad (6)$$

where C_s is the equilibrium W concentration in the soil, mg kg^{-1} , C_w the W concentration in water at equilibrium with a soil, mg l^{-1} and K_d is the soil–water partition coefficient, l kg^{-1} .

Experimentally determined values of soil–water partition coefficient are not readily available in the literature. Baes et al. [108], using an inverse relationship between the biocentration factor of W in plants determined experimentally and the soil–water partition coefficient, computed a $K_d = 150 \text{ l kg}^{-1}$, which is consistent with the lithophilic nature of W. Kerley et al. [107] argued that this value is overestimated and, using data from several occurrence studies, proposed a value of 30 l kg^{-1} . Using the data reported by Dermatas et al. [106] on four model soils described earlier, average K_d values (see Table 7) can be computed by linear regression analysis. The data do not depart markedly from linearity as evidenced by the R^2 values given on Table 7. On the other hand, adsorption appeared to better conform to Freundlich behavior according to:

$$C_s = K_F C_w^n \quad (7)$$

where K_F is the Freundlich isotherm constant ($\text{mg kg}^{-1}/(\text{mg l}^{-1})^n$) and n is the Freundlich isotherm exponential factor, dimensionless

Although theoretically more justified, the use of K_F is limited because of its dimensional complexity. A single-point K_d can be related to K_F by the following equation:

$$K_d = K_F C_w^{n-1} \quad (8)$$

Values of K_d varied in the range of 4.8 – 588.6 l kg^{-1} depending on the soil and the solution tested. These data confirm the lithophilic nature of W, however, the extent and nature of the adsorptive behavior is strongly influenced by soil and solution characteristics. Furthermore, for all solutions used, the adsorption of W appears to be strongest on the soil with the highest organic content (Pahokee peat), possibly indicating interactions with humic substances, an area worth of additional attention and study. Experimentally determined soil–water partition coefficients for natural systems and statistical correlations of this parameter to soil and solution characteristics are available in the literature for other metals but not for W [116,117]. A multitude of factors affect adsorption of metals on soils including nature

Table 7
Soil–water partition coefficients for dissolved W in four model soils (numbers in parenthesis represent regression R^2)

Soil type	W bearing solution (% alloying element)		
	W:Ni:Fe (90:7:3)	W:Ni:Co (93:4.7:2.3)	W:Ni:Fe:Co (93:4.5:1.5:1.0)
Montmorillonite	178.2 (0.924)	339.0 (0.749)	36.6 (0.931)
Illite	49.4 (0.948)	66.2 (0.944)	37.8 (0.924)
Sigma sand	4.8 (0.922)	28.4 (0.922)	51.7 (0.625)
Pahokee peat	188.1 (0.879)	588.6 (0.873)	460.19 (0.642)

of soil mineral surfaces (particularly the potential in the plane of adsorption and surface-charge density), solution characteristics (ionic strength, relative abundance and type of anions/cations and/or organic ligands, solution pH and solution metal concentration) and environmental factors (pressure, temperature and soil/solution ratio) [118]. However, most parametric models in the literature recognize pH as the dominant parameter affecting K_d , although normalization of this parameter with respect to the organic matter content has in some cases improved the quality of the model markedly [119]. The organic matter–water partition coefficient is related to the soil–water partition coefficient by the equation:

$$K_{om} = f_{om}K_d \quad (9)$$

where K_{om} is the organic matter–water partition coefficient, $l\text{ kg}^{-1}$ and f_{om} is the fraction of organic matter present in soil, dimensionless.

From soil systems (soil and soil solution), tungsten can be transported to the biotic domain via a variety of organism-specific uptake mechanisms. The magnitude of the uptake is directly related to the bioavailability and bioaccessibility of tungsten and this, in turn, is affected by speciation. In an aquatic environment, some W may be present in its oxoanionic form (WO_4^{2-}), as polyoxotungstates, sorbed onto particulate material (biotic or inert), or sorbed onto colloidal material (e.g. humic substances and clay colloids). The amount available to biotic matter is only a fraction of the total amount and, thus, the use of total metal concentration as a descriptor of bioavailability is debatable. For an in-depth treatment, the reader is referred to a number of references dealing with assessment of bioavailability and bioaccessibility of contaminants in general and metals in particular [120–122]. The concept of equilibrium partitioning (EqP) is used widely in the literature for describing biotic uptake. EqP essentially relies on thermodynamic equilibrium of a target chemical species between soil solution and biotic tissue. Applied to W, the bioconcentration factor is a EqP-based partitioning coefficient defined as:

$$\text{BCF} = \frac{C_B}{C_w} \quad (10)$$

where C_B is the equilibrium W concentration in biotic tissue, mg kg^{-1} , C_w the equilibrium aquatic concentration, mg l^{-1} (or mg kg^{-1}) and BCF is the bioconcentration factor, $l\text{ kg}^{-1}$ (or dimensionless).

Although there are known shortcomings of the EqP and, consequently, the BCF, the partitioning behavior of W to soft-bodied organisms (e.g. earthworms) and biotic species, for which ingestion is not a major uptake route (e.g. plants) should be fairly reasonable. Experimentally determined values of BCF for W are not available in the literature. Baes et al. [108] used reported experimental values of W concentration in vegetative and fruit tissue and via a transgressive procedure based on the values for Groups IV and V elements predicted a soil-to-plant concentration factor (CF) of 0.045. CF is defined as:

$$\text{CF} = \frac{C_{\text{plant}}}{C_s} \quad (11)$$

where C_{plant} is the W concentration in the edible part of the plant, mg kg^{-1} and CF is the soil-to-plant concentration factor of W, dimensionless.

Kerley, using reported soil and plant concentrations from three literature sources cited in Ref. [107], calculated a geometric mean of 0.3, an arguably more reasonable value for CF. From data reported in the literature [41] for *Eucalyptus melanophloia* and *Triodia* grasslands and soil W contents in metalliferous areas of North Queensland, Australia, concentration factors for these two species are 0.08 and 5.4, respectively. Concentration factors can also be computed from data reported in W toxicity experiments on rye grass, recently published by our group [98]. For soil concentrations in the range of 0.1–10,000 mg kg^{-1} , the leaf W concentration of rye grass varied between 5.7 and 13,535 mg kg^{-1} resulting in CI values in the range of 0.2–56.7. With the exception of the highest W leaf concentration (13,535 mg kg^{-1}), where toxicity was evident and resulted in a significant reduction of the plant's total mass, an inverse relationship between CF and W exposure concentration in the soil is evident. This relationship is highly linear ($R^2 = 0.956$) and is described by the following equation:

$$\log \text{CF} = -0.623 \log C_s + 0.956 \quad (12)$$

Similar inverse relationships between the BCF and exposure concentration were reported for several metals (Ag, Cd, Cu, Hg, Ni, Pb and Zn) and aquatic biotic species [99]. BCF and CF are interrelated via the following equation:

$$\text{BCF} = K_d \text{CF} \quad (13)$$

Concentration factors, computed from data reported in our W earthworm toxicity study [98], varied by one order of magnitude (0.02–0.2) for soil exposure levels in the range of 10–10,000 mg kg^{-1} soil. An inverse relationship between CF and exposure level cannot be validated in this case due to limited number of data.

Analogous to the CF is the use of the biota/sediment accumulation factor (BSAF) [123,124] developed to express equilibrium partitioning between sediment systems and biotic species, defined as:

$$\text{BSAF} = \frac{C_B}{C_{\text{SED}}} \quad (14)$$

where C_B is the W concentration in biotic tissue, mg kg^{-1} , C_{SED} the W concentration in the sediment or benthic material, mg kg^{-1} and BSAF is the biota/sediment accumulation factor, dimensionless.

In the quest for determining bioavailable and bioaccessible metal fractions and in order to address the multi-faceted nature and complexity of metal speciation in environmental systems, a number of partition coefficients have been suggested in the literature. In addition to the commonly used soil–water partition coefficient, databases and literature exist for several metals, but not tungsten, for particle/water, suspended matter/water, sediment/water and dissolved organic carbon/water coefficients [121,125].

Table 8
Summary of W partition coefficients for various environmental interfaces

Interface, unit	Value	Conditions/reference
Soil–water (K_d) ^a (l kg ⁻¹)	150	Calculated from literature values, reported by Ref. [108]
	30	Calculated from several literature data, reported by Ref. [107]
	4.8–589	Calculated from data by Ref. [106] reported here, details given in Table 6
Soil–organism (CF) ^b	0.045	Limited data from literature for vegetables and fruits, and transgressive procedure based on Groups IV and V elements, calculated and reported by Ref. [108]
	0.3	Various vegetables, fruits and plants, calculated from several literature sources, reported by Ref. [107]
	0.08	<i>Eucalyptus</i> leaves in metalliferous areas based on data published by Ref. [41], calculated and reported here
	5.4	<i>Triodia</i> grasslands in metalliferous areas based on data published by Ref. [41], calculated and reported here
	0.2–56.7	Rye grass based on data published by Ref. [106], calculated and reported here
	0.02–0.2	Earthworms based on data published by Ref. [106], calculated and reported here
	Animal feed–food product (BTF) ^c	0.00021
0.037		Beef meat based on data from various literature sources, calculated and reported by Ref. [107]
0.3		Chicken meat based on data from various literature sources, calculated and reported by Ref. [107]
3.0		Chicken eggs based on data from various literature sources, calculated and reported by Ref. [107]

^a Soil/water partition coefficient defined in Eq. (6).

^b Soil-to-plant concentration factor defined in Eq. (11).

^c Biotransfer factor for food product defined in Eq. (15).

The uptake of tungsten in animal food products is expressed by the biotransfer factor defined as [99]:

$$\text{BTF} = \frac{C_{\text{FP}}}{C_{\text{F}} Q_{\text{F}}} \quad (15)$$

where C_{FP} is the W concentration in animal food product, mg kg⁻¹, C_{F} the W concentration in the animal feed, mg kg⁻¹, Q_{F} the amount of feed consumed by the animal daily, kg day⁻¹ and BTF is the biotransfer factor for a food product, day kg⁻¹.

BTF is used for the determination of daily W intake by food ingestion in human exposure studies. Kerley et al. [107] using bibliographical information calculated, the BTF of milk, beef meat, chicken meat and egg to be 0.00021, 0.037, 0.3 and 3.0, respectively. These preliminary BTF values indicate that small to moderate amounts of tungsten can be taken up by consumption of animal produce. A summary of available partition coefficient found in the literature is given in Table 8.

4. Toxicology/environmental medicine profile

Toxicological information on tungsten and its compounds is limited in comparison to other metals. Available data relate primarily to pharmacokinetics of tungsten in humans and animals, and to a lesser degree to mechanisms of toxicity. Prompted by the leukemia cluster events, CDC requested a full toxicological study for tungsten and related compounds [10]. An extensive review of the toxicological literature on tungsten and its compounds was recently published by the National Institute of Envi-

ronmental Health Sciences (NIEHS) [11] and then updated by the Committee on Updating of Occupational Exposure Limits of the Health Council of The Netherlands [126]. Ingestion of beverages is the main route of tungsten exposure for the population at large. Inhalation of dusts and dermal contact are the principal routes of occupational exposure. Table 9 summarizes tungsten levels in various human body organs of healthy individuals.

Traditionally, health, safety and toxicity of tungsten and tungsten compounds were viewed as non-problematic as there have rarely been documented cases of tungsten poisoning in humans

Table 9
Tungsten levels in various organs and fluid streams of healthy individuals (compiled from information from Ref. [11] unless otherwise noted)

Matrix	Concentration, $\mu\text{g kg}^{-1}$ (unless otherwise noted)
Bone	0.25
Hair	16
Heart	2
Plasma	<0.7 mg l ⁻¹
Serum	<0.7 mg l ⁻¹
Skin	26–160
Tooth enamel	240
Tooth dentine	2600
Urine	<32 μg
Urine concentration geometric mean U.S. population (>6 years old) [127]	0.085 $\mu\text{g l}^{-1}$
Urine concentration 50th percentile U.S. population (all ages, both sexes) [128]	0.90 $\mu\text{g l}^{-1}$

[129]. Several exposure and epidemiological studies in the workplace, cited in a NIOSH publication as part of the background for establishing OSHA limits [23], provide indications of a possible role for metal tungsten and tungsten carbides in “hard metal disease”, a condition that may often be followed by pulmonary fibrosis. Several studies contain indications of adverse health effects on humans and propose prevention measures to eliminate exposure to tungsten oxide fibers and tungsten dust in the workplace [56,130]. A case of tungsten poisoning in the French Army has been documented in the literature [131,132]. A young soldier developed seizures and tubular necrosis after drinking a small amount (about 250 ml) of a beverage prepared by rinsing still gut-barrels with wine. Tungsten, present in the wine in a high concentration (1540 mg l^{-1}), was also detected in gastric content (8 mg l^{-1}), serum (5 mg l^{-1}) and urine (101 mg l^{-1}) of the soldier. This case initiated a public discussion about possible tungsten neurotoxic activity that was up to that point unknown [133]. The alternatively proposed reason for the poisoning by 1,3,5-trinitro-1,3,5-triazine (hexogen or RDX) was rejected [134].

Acute toxicity of tungsten had been studied in various laboratory animals. According to a recent review [135], the median lethal dose (LD_{50}) by subcutaneous injection was determined to be 71 mg W per kg in rabbits, by intraperitoneal injection 80 mg W per kg in mice and 112 mg W per kg in rats. The following lethal doses were determined by intravenous introduction: 463 mg W per kg for dog, 272 mg W per kg for chicken, 154 mg W per kg for rat, 128 mg W per kg for pigeon, 79 mg W per kg for cat and 59 mg W per kg for rabbit. Acute oral and intravenous toxicity of sodium tungstate (reported as LD_{50}) in rats (1928.4 and 61.9 mg kg^{-1} , respectively) and in mice (1904.1 and 107.1 mg kg^{-1} , respectively) were reported by Domingo [136]. In general, these LD_{50} values indicate that tungsten compounds have a relatively low toxicity, in comparison to other heavy metals (i.e. vanadium) that are under evaluation as possible antidiabetic agents. Acute W intoxication produces a variety of symptomatic signs depending on the target animal and administered route of exposure including asthenia, adynamia, prostration, coma (intraperitoneal injections in rats and mice), anorexia, colic, disorganized movements, trembling and dyspnea (oral administration in guinea pigs) [135].

Chronic toxicity studies showed that sodium tungstate given orally for 4 (subacute) and 13 (subchronic) weeks to young rats or dogs at doses in the range of $15\text{--}1000 \text{ mg kg}^{-1}$ per day produced emesis, anorexia, cachexia, pallor and dyspnea; additionally, higher doses caused an increase in urea, creatinine and total cholesterol, and a decrease in glucose, protein, erythrocytes, hematocrit and hemoglobin levels [136–138]. All parameters returned to normal levels upon exposure interruption after a recovery period of 6 weeks [137,138]. An earlier study reported a statistically significant decrease of longevity in rats who were given sodium tungstate in drinking water [139]. However, in a more recent study degradation of implanted tungsten coils in the subclavian artery of New Zealand white rabbits in a long-term study (4 months) did not produce chronic or systemic toxicity, but the tungsten level in serum rose from $0.48 \text{ } \mu\text{g l}^{-1}$ prior to implantation to $12.4 \text{ } \mu\text{g l}^{-1}$ 4 months after implantation [140].

Recent *in vivo* studies demonstrate possible cytotoxic, genotoxic and carcinogenic effects of tungsten based implant materials. Cytotoxic effects from degradation of the tungsten coils was demonstrated on human pulmonary arterial endothelial (LD_{50} of $50 \text{ } \mu\text{g ml}^{-1}$), smooth muscle cells (LD_{50} of $100 \text{ } \mu\text{g ml}^{-1}$) and human dermal fibroblasts (LD_{50} of $1000 \text{ } \mu\text{g ml}^{-1}$) after 10 days of incubation [141]. Tungsten and a reconstituted tungsten/nickel/cobalt mixture, simulating tungsten alloys used in military applications, have been shown to activate gene expression through several signal transduction pathways that may be involved in oncogenicity [142]. Genotoxic effects for various tungsten compounds, including tungsten carbide, sodium tungstate, tungsten(IV) oxide, tungsten(VI) chloride, and its products of microparticle decomposition, have been demonstrated in experiments with human cells [143,144]. However, the mechanism appears not to be related to DNA nicking [145]. Cemented carbides consisting of tungsten carbide and metallic cobalt were shown to be genotoxic in human lymphocytes and in type II pneumocytes producing DNA strand breaks and micronuclei directly associated with risk of lung cancer in occupational settings [146].

Kinetic models of tungsten distribution and retention in humans [147] and animals [148,137,138] have been proposed based on a variety of animals (i.e. dogs, cows, sheep, goats and rodents), tungsten exposure levels and routes [147,148]. Radio-tungsten ^{185}W compounds introduced to animals by injections, ingestion or inhalation [147] initially resulted in accumulation of a substantial portion of deposited tungsten in blood soft tissues, but the initial burden lost within a few hours [135]. Tungsten usually accumulates in liver, spleen, skeleton and kidneys [147], and, also, in the lungs when $^{181}\text{WO}_3$ is inhaled [149]. Tungsten concentrations appear to be higher in the liver than in other soft tissue organs of animals irrespectively of the method of metal exposure [150,151]. These results can be explained by the ability of tungsten to inhibit or to replace the molybdenum in different liver enzymes, such as xanthine oxidase, xanthine dehydrogenase and sulfur oxidase [152]. Typically most of the introduced tungsten is fast excreted to urine and intestinal content [148], however, long-term retention of tungsten in bone has also been reported [135].

5. Discussion and conclusions

Tungsten and most of its compounds have traditionally been considered as substances of limited environmental liability. However, recent events reviewed here, implicating tungsten in ALL clusters, have disrupted a pattern of environmental obscurity for tungsten and its compounds signifying an era of environmental scrutiny. This is evident by a surge in recent environmental publications as well as by recent activities of health, environmental and regulatory agencies in the U.S. and other countries. The discussion that follows outlines areas where information ambiguity and/or knowledge gaps exist justifying additional study and research for a clear and complete environmental profile for tungsten and its compounds.

The sources of most occurrence data presented either represent estimates in referenced literature or are derived from

studies whose focus is other than occurrence. Consequently, most occurrence information is of incidental and local character. Relatively well-characterized terrestrial systems in terms of occurrence are areas bearing tungsten deposits and locations of high hydrothermal activity. Very limited information, however, exists for terrestrial systems of potential anthropogenic contamination. Terrestrial systems in need of characterization include: (a) sites of military activity (firing ranges and combat fields) where W-based hardware is used (e.g. munitions and penetrators), (b) hunting grounds where W shots are fired in migratory bird hunting, (c) agricultural soils where application of fertilizers containing W are applied, (d) soils in proximity to smelting and metals processing facilities, (e) soils in the proximity of or exposed to runoff from high-traffic roadways and highways, (f) sites of land application of wastewater residuals, (g) municipal and industrial solid waste streams and (h) active and closed municipal and hazardous waste landfills.

Although W is a lithophilic substance atmospheric enrichment is evident in industrial and urban areas. W occurrence in particulate and aerosol atmospheric fractions is confirmed and reported in the existing literature. Better characterization and monitoring is essential for emission streams from incineration facilities, coal-fired power plants, metal smelting/mining facilities and landfill gases. Attention should also be paid to industrial facilities and processes involved in production of tungsten based nanomaterials, and tungsten oxides used in electro-optical, electrochromic, ferroelectric, catalytic and semiconductor applications.

Although W has traditionally been regarded as a substance of limited aquatic solubility and mobility, a substantial enrichment is observed in natural aquatic systems, both surface and underground, in close proximity to areas of W-bearing mineral deposits and hydrothermal activity. Caution must be minimally exercised when communities use these water resources and treatment is imperative before use as a public water supply. At a local scale, occurrence data and systematic characterization studies are essential for surface waters in areas near or on hunting grounds and fishing rivers and lakes where W fishing weights are used. Careful monitoring and characterization is also essential for liquid waste streams from smelting and metal processing facilities, leachates from municipal and hazardous waste landfills, and agricultural and roadway runoff. At a regional level, systematic characterization studies and monitoring are important for big river systems flowing through basins of intense mining, agricultural or industrial activity.

The role of tungsten in biological systems has only been established recently in contrast with its chemically close relative Molybdenum whose biological role has been known for decades. The effects of tungsten in biotic systems reported in the literature range from beneficial to moderately toxic with more recent studies leaning towards the latter. Tungsten appears to be taken up in various amounts by plant organisms covering the entire spectrum from excluders to hyperaccumulators. Some data are available for wild plant species, whereas only limited data exist on food crops. Upon uptake from soils, water or atmospheric systems, plants appear to have the capability to translocate W to various parts of their anatomy. Although a limited number of

studies have suggested possible uptake, sequestration and toxicity mechanisms in plants, this is definitely an area worth of additional experimental research. Biomagnification and release of sequestered W back into the environment is another area where additional research is needed.

The environmental chemistry of tungsten is also an area in need of immediate research attention. Knowledge gaps exist with respect to basic properties (physical, chemical, biological and thermodynamic) for a number of W compounds, severely limiting modeling ability both at the prediction and experimental planning levels. Speciation of tungsten in aquatic systems is another area with ample room for basic research. Currently, W speciation in water as a function of pH is either purely theoretical or modeled with no experimental validation. Recent advances in analytical chemistry may offset some of the complexities arising from the multiple oxidation state/coordination number nature of W. The ability of W to polymerize in acidic environments is of high relevance to bioavailability as W isopolytungstates appear to represent the free metal (toxic) form facilitating application of EqP or the biotic ligand (BLM) speciation models. Interactions of W with DOM, specifically the dissolved fulvic and humic acid fraction as well as the conditions leading to formation of organotungsten compounds are areas where minimum research activity has been documented, although, for the latter, tungsten hexacarbonyl, an organotungsten precursor, has been detected in landfill gases. Additional environmental chemistry areas of relevance to speciation, bioavailability and fate and transport issues where some research has been performed but additional research is certainly needed, include competitive adsorption, complexation and precipitation.

In terms of fate and transport across environmental interfaces, tungsten is probably one of the most poorly studied metals. With the exception of some very recent preliminary studies, there have been no fate and transport studies in the literature. The partitioning behavior is currently determined based on coefficients that are either estimates or based on scarce incidental occurrence data, for which equilibrium conditions are not verifiable. Concentration and bioconcentration factors are limited both in terms of numbers and number of species (primarily plants), thus making it impossible to assess the bioaccumulation and biomagnification potential for tungsten and its compounds. Basic laboratory research is needed for assessing fate and transport of W both in controlled and natural environments.

The toxicological profile of tungsten and related compounds is sketchy and fragmentary. The available literature concentrates primarily on pharmacokinetics of tungsten in humans and animals and, to a much lesser extent, on toxicity mechanisms. Several acute and chronic toxicity studies have been conducted on a variety of laboratory animal subjects via multiple exposure routes. Areas of additional research should include immunological, neurological, reproductive/developmental and carcinogenic effects. Toxicology and carcinogenesis studies are currently under way as a result of tungsten being nominated to the National Toxicology Program (NTP).

In summary, it appears that environmental obscurity for tungsten and its compounds has ended and environmental scrutiny has emerged. With regulation imminently approaching,

treatment of W-bearing waste streams and remediation of contaminated environmental matrices along with environmental management, life cycle assessment, pollution prevention and recycling/reuse may well be additional areas of high research demand.

Although the reviewed body of interdisciplinary literature has not always been convincingly conclusive about the environmental relevance of tungsten and its compounds, the indications presented cannot in anyway justify a benign neglect approach. On the contrary, a more proactive approach is needed based on the precautionary principle. Additional basic research in order to provide clear answers to a number of unresolved issues ranging from occurrence, to environmental chemistry, to fate and transport and toxicology and possibly scientifically justified regulation is urgently needed.

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