Review

The Dynamics of Tungsten in Soil: An Overview

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Abstract: The increasing use of tungsten in the production of green energy in the aerospace and military industries, and in many other hi-tech applications, may increase the content of this element in soil. This overview examines some aspects of the behavior of tungsten in soil, such as the importance of characteristics of soils in relation to bioavailability processes, the chemical approaches to evaluate tungsten mobility in the soil environment and the importance of adsorption and desorption processes. Tungsten behavior depends on soil properties of which the most important is soil pH, which determines the solubility and polymerization of tungstate ions and the characteristics of the adsorbing soil surfaces. During the adsorption and desorption of tungsten, iron, and aluminum oxides, and hydroxides play a key role as they are the most important adsorbing surfaces for tungsten. The behavior of tungsten compounds in the soil determines the transfer of this element in plants and therefore in the food chain. Despite the growing importance of tungsten in everyday life, environmental regulations concerning soil do not take this element into consideration. The purpose of this review is also to provide some basic information that could be useful when considering tungsten in environmental legislation.

Keywords: tungsten; soil properties; bioavailability; plant uptake

1. Introduction

Tungsten (W) occurs naturally in soils and the Earth's crust is the most important source of this element. Tungsten reserves have been estimated to be approximately 3.1 Mt [1] in ore deposits, where the metal exists mainly as a component of several minerals, such as wolframite (Fe, $MnWO_4$) and scheelite ($CaWO_4$) [2].

Until quite recently, the behavior of tungsten in the soil did not receive particular scientific interest. This stemmed from the belief that tungsten was substantially inert in the environment and relatively insoluble [3,4]. Moreover, although some sporadic studies reported that tungsten could be solubilized under particular conditions of pH and redox potential [5–10], the lack of adequate analytical techniques at that time meant that tungsten was merely cited as being similar to molybdenum, but without its essential properties being thoroughly investigated. In reality, tungsten can be solubilized and can be mobilized in the soil environment and can be leached to ground waters [5–9].

Tungsten has drawn increased attention after the discovery of high levels in several environmental compartments. Concern over tungsten started with the cases of three sites in the west of the United States, were the metal was attributed to being a potential source of the childhood leukemia clusters [11–18]. Nowadays, the USEPA has included tungsten compounds in the National Priorities List [19] with particular consideration to poly-tungstates.

This overview briefly describes some aspects of the retention, mobility, and bioavailability of tungsten in soils. The aim is to contribute to the knowledge of tungsten, as well as to improve soil legislation. In fact, the increasingly massive use of tungsten in industrial products has led to a consequent increase in its concentration in soils. As a result, new environmental problems may arise, which, only a few years ago, were completely unthinkable.

2. Production and Uses of Tungsten

Low-carbon technologies are fundamental to achieving sustainable growth based on energy production from renewable sources, with fewer CO_2 emissions and more efficient energy consumption. These technologies use the physical and chemical properties of some metallic elements as fundamental components in engines and batteries in green production processes. Tungsten increases the efficiency of clean and renewable energy techniques that serve as alternative to fossil fuels [20].

The main issues in the production of green energy are linked to the limited availability of certain critical metals, including tungsten. Critical metals are defined as those elements that are indispensable for the functionality of low carbon technologies, but are expensive and have potentially unstable supplies. Moreover, political and environmental effects induced by a growth in demand highlight a clear discrepancy between consuming and producing countries [21].

In 2020, an estimated 84,000 metric tons of tungsten were produced globally. China is, by far, the world's largest producer since the largest deposits of tungsten ores, 60% of worldwide reserves, are located in China. In the EU, Austria (with the Mittersil mine), and Portugal (with the Panasqueira mine), are the biggest tungsten producers [22].

There are serious concerns that the increase in green technologies by countries that are trying to limit their greenhouse gas emissions will inevitably and paradoxically increase demand for metals, such as tungsten. On the one hand, there is a risk of shortage in the tungsten supply and, at the same time, the global flow of tungsten could impact on environmental matrices derived from increased production and use.

In a seminal article from fifteen years ago by Koustopyros et al. [13], tungsten was defined as "a relatively known transition metal", but "of high strategic importance for the years to come". Today, due to its wide use in high-tech industries and in low-carbon applications [23], tungsten is internationally considered to be a "critical metal" [24–27].

Tungsten has the highest melting point of all metals (3422 $\pm$ 15 °C) and the lowest vapor pressure. With a density of 19.25 g cm^{-3}, tungsten is also among the heaviest metals. Due to its thermal and chemical stability, it is the key metal for thermo-emission applications. Due to its peculiar properties, including its very high hardness, tungsten is irreplaceable in several industrial and military applications [28]. Tungsten-based materials are envisaged in future nuclear reactors to withstand the high energies required and the repeated impact of significant thermal loads [29]. Tungsten is crucial for emerging technologies and is of increasing major economic importance [30].

The procedure used to track the fate of an element throughout its life cycle, recognizes, for tungsten, some primary life stages (Figure 1): mining, production, fabrication and manufacturing, use, waste management, and recycling [22].
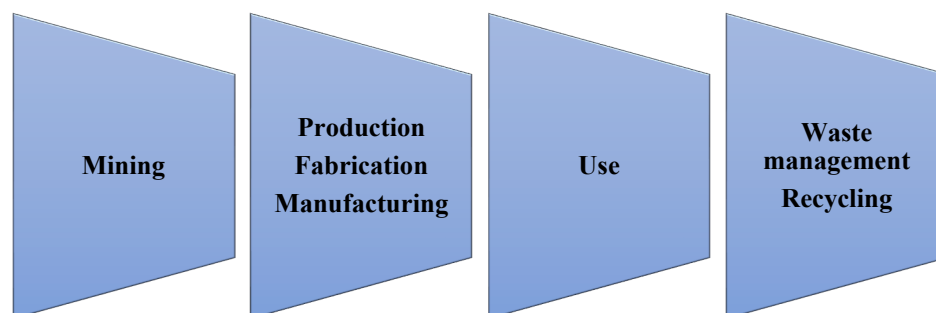
Figure 1. Schematic diagram of tungsten flow analysis.

In the manufacturing and fabrication phases, in which products containing tungsten that are requested by the market are prepared, the production of dust and atmospheric transport must be considered as an important environmental issue, also in terms of deposition of airborne particles on soils [15].

Regarding the use phase, concerns have been raised about military applications of tungsten [31] in the production of tungsten/nylon bullets under the US Army's Green Armament Technology Program as substitutes for lead-based munitions [32]. Millions of tungsten/nylon bullets have been produced [33].

Tungsten is also used in large amounts in optical and photovoltaic applications, nanomaterials, catalysts to produce hydrogen [34], and numerous household products; thus, increasing amounts of tungsten residues are being generated. Tungsten is also being spread in the environment and through soils by municipal sewage sludge, solid waste, and landfill leachate [13].

During manufacturing and usage, the release of tungsten due to emissions (e.g., aerosolization) can result in increased concentrations in soils surrounding facilities [35,36], while products containing tungsten can release the metal into the environment due to wear and tear. Due to concern about human health, the spatial trends of airborne tungsten have been investigated using technologies such as wavelength-dispersive spectrometry and transmission electron microscopy [15]. Nano particles of composite metals, such as tungsten carbide cobalt (WCCo), are increasingly being produced and have key mechanical properties for mining and drilling industries [37].

In a circular economy, the main raw material for tungsten production in the future should ideally derive from the high quantities of tungsten scrap [22,38]. The management of waste and tungsten reusage will affect various environmental sectors, including soil.

3. Influence of Soil Properties on Tungsten Chemistry

The natural concentrations in soil range from 0.1 to 5 mg kg^{-1} [39]; however, in specific areas, such as war zones, firing ranges, and mining sites, tungsten concentrations can be from 10 to over 1000 times than that of natural uncontaminated soils [40]. In some soils at military installations, a tungsten concentration of up to about 3000 mg kg^{-1} has been discovered in surface horizons [13,31,33]. In mining phases, where tungsten is extracted from ores, the tungsten concentration in soils surrounding these areas can reach values higher than 1000 mg kg^{-1} [41–44]. Contamination in soils from these areas has resulted in tungsten entering the plant ecosystem, with negative consequences for the food chain [45]. High tungsten concentrations have also been discovered in soils in the vicinity of mining/smelting sites (from about 50 to about 80 mg kg^{-1}) in North Queensland (Australia) and Nevada (USA) [46].

Due to fertilization with phosphate fertilizers, which contain tungsten, agricultural soils in the European Union have also reported concentrations close to 100 mg kg^{-1}, which are thus much higher than those of natural soils [47]. Agricultural practices have been considered as a source of higher content in some agricultural soils of New Zealand, from 1.9 to 21.4 mg kg^{-1} [13].

High tungsten contents (126 mg kg^{-1}) have been reported in surface soils of Gulf War (1990–1991) zones close to the Saudi Arabian–Kuwait border [48]. In the USA, in military shooting areas, due to the use of tungsten-based ammunition, the tungsten concentration in soils ranged from 5200 to 5500 mg kg^{-1} [40,49].

The behavior of tungsten depends on the specific characteristics of the soils that regulate its distribution between the liquid and the solid phases. In soil, its oxidation state ranges from −2 to +6, the most common of which is +6. In fact, in soils, tungsten occurs mainly as tungstate anion (WO_4^{2-}), which is thermodynamically very stable [13]. However, the dynamics of tungsten in soil are complex due to its tendency to form polymers, even with other ions present in the soil, such as phosphates and silicates (Figure 2).
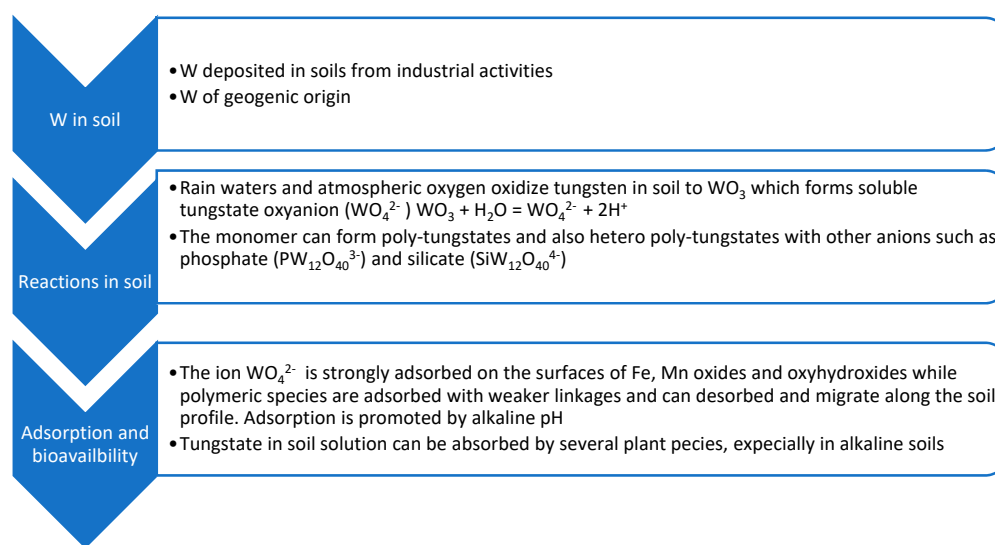
Figure 2. Schematic reactions of tungsten in soil.

Poly-tungstates are formed from the tungstate monomer, including stable polyatomic anions, such as $H_2W_{12}O_{40}^{6-}$, $HW_6O_{20}^{3-}$, and $W_6O_{20}(OH)^{5-}$. These tungsten (VI) species are stable in more concentrated and acidic solutions, while the monomer is more stable in dilute and basic solutions [50].

Tungstate monomer can also form several cluster compounds that contain two or more metal atoms polyoxometalates (POMs) that are built of WO_6 and a central XO_4 tetrahedron. These POMs have not been definitively identified in soils, nor is their stability known; however, these polymers likely play a key role in environmental systems. The polymeric forms of tungsten appear to be soluble and mobile in soils [50]. Tungsten tends to oxidize in relatively short times to tungsten (VI), reacting with water in soil; consequently, some metal in a soluble form is released into the soil solution [31].

In soil samples collected from military firing ranges where tungsten ammunition had been used for several years, XANES spectroscopy revealed that 98% of the tungsten was present as tungsten (VI), with an extremely low presence of metallic tungsten. In accordance with the XANES data, EXAFS spectroscopy highlighted that tungsten was present essentially as poly-tungstates and/or POM, particularly in the surface layers [50].

Soil characteristics (pH, organic matter, etc.), as well as the intrinsic properties of tungsten compounds, determine the distribution in various pools of bioavailability:

- In soil solution as simple or polymeric soluble ions;
- Adsorbed on mineral particles in exchangeable forms, forming outer sphere complexes;
- Adsorbed on oxides and hydroxides forming inner sphere complexes;
- Adsorbed or complexed by organic matter;
- Included in the crystal lattice of soil minerals.

The first two pools are the most important in terms of releasing available forms of tungsten for plants, while the other three pools are characterized by a decreasing availability (Figure 3).

Soil chemistry assesses the distribution of metal in the various pools. For heavy metals present in a cationic form, there are various sequential extraction procedures (SEP) that can be used; for tungsten, it is necessary to select extractions for a metal present in the anionic form. A comparison with the Tessier SEP [51], which is often used for cationic metals, showed that the sequential extraction scheme used by Wenzel [52] for the study of arsenic was also the most appropriate SEP for estimating tungsten mobility and bioavailability [53].
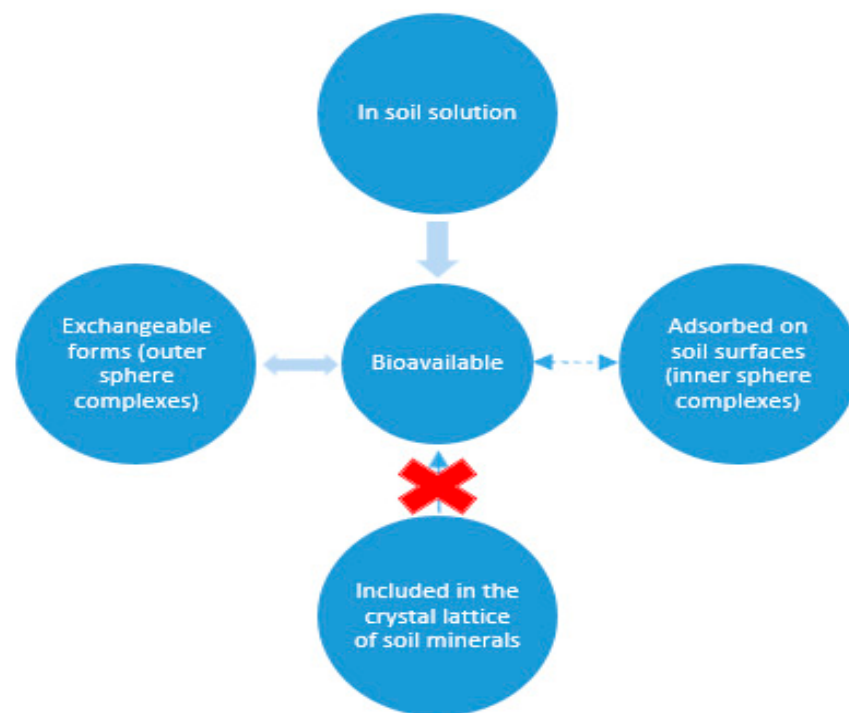
Figure 3. Conceptual model of bioavailability of monomeric and polymeric forms of tungsten.

The Wenzel scheme identifies five fractions into which tungsten can be subdivided: non-specifically adsorbed (F1), specifically-adsorbed (F2), linked to poorly-crystalline and amorphous hydrous oxides of Fe and Al (F3), linked to well-crystallized hydrous oxides of Fe and Al (F4), and a residual fraction not involved in the environmental processes (F5).

With regard to the Wenzel SEP, the concentration of tungsten in the F1 fraction extractable by 0.05 M $(NH_4)_2SO_4$ represents the soluble and exchangeable forms of the element, and thus the readily labile amount that has the highest environmental risk. The F1 fraction also indicates quantities that may be bioavailable to plants; however, an accurate description of this quantity can also be obtained by a single extraction with water [54] or 0.01 M calcium chloride [55].

The concentration of tungsten in the F2 fraction, extractable by 0.05 M $NH_4H_2PO_4$, indicates the specifically adsorbed amounts that may be considered potentially mobilized due to changes in some soil conditions, such as the pH value.

The concentration in the F3 fraction, extractable by 0.2 M NH_4-oxalate buffer (pH 3.25), represents the tungsten linked to poorly crystalline and amorphous hydrous oxides of Fe and Al. The objective of the oxalate reagent is the dissolution of amorphous Fe oxyhydroxides.

The concentration of tungsten in the F4 fraction, extractable by 0.2 M NH_4-oxalate buffer + 0.1 M ascorbic (pH 3.25), provides an estimation of the amount linked to well-crystallized hydrous oxides of Fe and Al. The oxides/hydroxides of Al, Fe, and Mn are the main tungsten sinks for environmental processes [56–58].

The concentration in the F5 fraction, extractable by HF–HNO$_3$–HClO$_4$ (*v/v/v* 1:3:2) at 180 °C, represents the metal included in the crystal lattice of soil minerals.

Even though the Wenzel's SEP is the most used for tungsten, it is not the only one. A different sequential extraction has been used to define tungsten speciation in mining soils [59]. This procedure, originally used by Dold [60], subdivided tungsten forms into seven fractions: (1) poly-tungstates water-soluble phase, (2) exchangeable phase, (3) easily reducible minerals, (4) resistant reducible minerals, (5) easily oxidizable minerals, (6) resistant oxidizable minerals, and (7) residues and silicates.

Whichever SEP is used, most of the tungsten is generally recovered in the last residual phase, which shows the chemical form of tungsten that is most strongly retained by soil solid components. These residual fractions pose the lowest environmental risk [53,54].

As is known, any sequential extraction only operationally defines the different forms of an element, in this case, tungsten, because the results obtained depend on the choice of the extracting agent and the operating methods of the extraction [61]; however, sequential extraction procedures are a simple way to assess potential bioavailability, because they identify, on an increasing scale, the different bond strengths with which tungsten is retained by soil surfaces.

The distribution of tungsten in the various extractable fractions is determined by the characteristics of the soil, in particular: pH, organic matter, and oxi-hydroxides.

As with all other metals [62], soil pH plays a crucial role in determining the mobility and bioavailability of tungsten. Tungstate ion behaves similarly to molybdate, and by increasing the solubility, it becomes more bioavailable as pH increases [55,63,64]. The solubility of tungstate is strongly influenced by interactions with the positively charged surfaces of minerals, such as those of metal oxides (Fe, Al, Mn), of which the surface charge is controlled by the pH of the soil, and those of the external sites of clay minerals [65]. As pH increases, the mobility of tungsten increases, with possible leaching [63]. These aspects are fundamental in the rhizosphere because the influence of the roots on the surrounding soil is particularly important for the release of protons or hydroxyl ions, which can modify the pH value in this microenvironment [66].

Under certain geochemical conditions, tungstate tends to polymerize. This process is favored by acidic pH values, and also by higher tungsten concentrations [8,64].

A few studies have investigated the interactions between tungsten compounds and organic matter in soil. Soils with a high content of natural organic matter generally have a greater capacity to adsorb tungsten than soils with a lower organic matter content. The importance of the formation of tungsten complexes with organic matter has been highlighted in a comparison involving peat, kaolinite, and montmorillonite. The adsorption of mono-tungstates followed the following order: peat > kaolinite > montmorillonite > illite [67]. In soils of the Mediterranean region, the content of humic materials is one of the most important soil properties that can reduce the mobility of tungstate [68,69]. Interactions between WO_4^{2-} and humic substances reduce tungstate mobility, due to adsorption reactions [63]. Interactions of tungsten with humic substances largely depend on soil pH. The increase in pH, from acid to alkaline, increases the mobility of tungsten due to WO_4^{2-} anion formation.

The interactions of tungsten with organic matter may be enabled by the presence of amino groups, due to their positive charge. Similar to arsenate [70], tungstate may be linked indirectly to organic matter by bridging with hydrolytic species of Al and Fe detained on humic substances forming ternary tungsten complexes. The affinity of organic matter for soluble tungsten compounds seems to hinder tungsten from leaching into the soil system [71]. Laboratory studies suggest that although the monomer has a higher adsorption rate than poly-tungstate, the latter is preferentially sorbed to rich organic soils, decreasing migration along the soil profile [72].

However, conflicting results that derive from the interaction of humic substances with the surfaces of the hydroxides must also be considered. The surfaces of these minerals can be coated with organic matter, and this coating appeared to reduce adsorption processes. In presence of high concentration of humic materials, X-ray photoelectron spectroscopy (XPS) showed the formation of an inner-sphere of tungsten monomer complexes on iron hydroxides, and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) demonstrated, in presence of humic materials, an increase in polytungstates that are weakly adsorbed and, thus, more mobile than tungstate monomer [73].

The reactivity of tungsten in soils is strictly related to the presence of iron(hydr)oxides and non-crystalline aluminum silicates. In fact, tungstate is strongly adsorbed onto the surfaces of these variable charge minerals and also on carbonates and at the edges of phyllosilicates. Tungstates adsorb on different surface sites in soils, forming loosely and strongly bound surface species, which may also be in a polymeric form. Tungstates that are specifically adsorbed, form inner-sphere complexes replacing $-OH^-$ or $-OH_2$ groups

from the surfaces of variable charge minerals. Different surface complexes may be formed on inorganic soil components, depending on the pH and surface coverage [70].

Several types of hydroxyl groups (basic, neutral, and acidic) are involved in the linkage of the differently bounded species. FTIR, Raman spectroscopy, TPR and EXAFS have shown that tungstate adsorption on oxo-hydroxides is due both to electrostatic bonding to protonated surface hydroxyls and to a reaction between tungstate and neutral/acidic OH groups. In the last case, the reaction can be considered as nearly irreversible [74].

Adsorption and Bioavailability

The immediate source of tungsten that is available for biological processes in soil, including plant uptake, is the amount present in the soil solution. This quantity is determined by the solubility of tungsten compounds and is controlled by the actual concentration in the soil solution and the quantity weakly adsorbed on soil surfaces and easily releasable in the desorption processes. The sorption processes determine the environmental behavior of tungsten in soils and its bioavailability to plants. These processes are governed by attractive and repulsive forces between soluble tungsten species and the soil solid phases. Depending on the characteristics of the attractive forces, tungsten is involved both in physical sorption and chemical sorption.
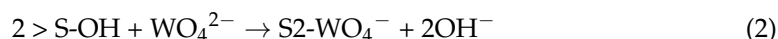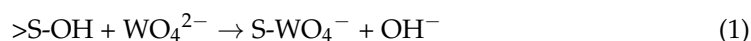
The mechanisms that regulate tungsten sorption in soil can be examined through sorption isotherms, which describe the retention of tungsten on the soil solid phase. The isotherms used in soil chemistry are an essential tool to evaluate the distribution of a substance between the solid and liquid phase and, thus, its bioavailability to plants.

To evaluate the retention/release process of tungsten in soil, several equations are used [68,75]. Although these equations ideally refer to a state of equilibrium and in soils, most of sorption processes are not fully reversible, and they describe the process and provide information on the bioavailability of tungsten.

Considering the adsorption of tungstate ion, the Langmuir and the Freundlich equations have been successfully used to describe the nonlinear sorption processes, both for mono and poly-tungstates in several soils [67,75].

Studies on tungsten adsorption in soils [75] showed that at low additions of tungsten, strong inner-sphere complexes of tungstate are formed, which are characterized by a near irreversible sorption, while with higher additions of tungstate the anion is more loosely linked and can be released by exchanging reactions. This behavior has also been reported for anions similar to tungstate, such as arsenate [76], molybdate [77], and phosphate [78]. The same conclusions were also reached regarding the adsorption of tungsten and molybdenum on aluminum oxides [74].

Similar to molybdate and phosphate, tungstate adsorption on variably charged soil surfaces can be described according to the following reactions [65,67,75].

$$>\text{S-OH} + \text{WO}_4^{2-} \rightarrow \text{S-WO}_4^{-} + \text{OH}^{-} \tag{1}$$

$$2 > \text{S-OH} + \text{WO}_4^{2-} \rightarrow \text{S2-WO}_4^{-} + 2\text{OH}^{-} \tag{2}$$

where WO_4^{2-} is the tungstate anion and >S-OH is a reactive metal hydroxyl group.

Concerning bioavailability, desorption processes are just as important as those of adsorption, since they define the amount of the metal that can be leached by soil surfaces. Relatively few data are available on the desorption of tungsten forms from soil or soil components.

Desorption experiments with soils with different characteristics [69] showed that, as in the case of the adsorption, soils characteristics influence the release of the metal from the soil surfaces. The amount of desorbed tungsten increased with increasing pH of the soils, and was also inversely related to organic matter content. Irrespectively of the different characteristics of the soils investigated in this experiment, the results showed that when added at low concentrations, the adsorption of tungstate mainly involved inner-sphere complexes and the percentage of releasable metal was very low (about 1–2%).

At increasing concentrations of added tungstate, the higher desorption indicated the occurrence of outer-sphere complexes with an increasing percentage of releasable metal (from 11 to 44%) going from the acidic to the more alkaline soil [69]. This adsorption/desorption hysteresis of tungstate has also been described for many inorganic and organic compounds in soil [79–82]. At acidic pH, desorption is lower and the amount of metal adsorbed, but not desorbed, can be reasonably considered to be in a form not available to plants.

4. Plant Uptake

Tungsten uptake by plants first gained attention through a study on health effects reported in the case of Fallon City [16,82]. Like other metals, tungsten is uptaken by the roots and translocated to the shoots via the xylem. In the roots, the tungsten concentration is higher than in the above ground parts of the plants [42,83].

The studies on the effect of tungsten on plants seem to indicate that tungsten in the soil is bioaccumulated in plant tissues, with consequent effects on growth and on some physiological parameters [84]. Studies conducted on *Lolium perenne* have shown negative effects on germination and plant growth [85]. Negative effects were detected only in the presence of very high concentrations of tungsten $\geq$10,000 mg kg^{-1} in soil [86]. In relation to the concentration of tungsten in the soil, significant physiological effects were found in sunflower, where "chlorophyll a" increased up to a concentration of 3900 mg kg^{-1} of tungsten in the soil, but it dramatically decreased at higher concentrations, while carotenoids increased significantly at tungsten concentrations above 3900 mg kg^{-1} [87]. The effects have been attributed to a compensatory mechanism for the stress induced by tungsten in analogy with copper [88].

There are several possible mechanisms through which tungsten induces stress phenomena in plants, in particular the lowering of the pH in the rhizosphere with consequent variations in the bioavailability of nutritional elements, such as phosphorous and nitrogen. Furthermore, the formation of tungstate polymers with phosphates can modify the availability of phosphor for plants with a consequent exhaustion of the intracellular reserves of phosphate [82]. This then alters the phosphorylation reactions in cells, including the cellular signaling pathways [87]. Tungsten in soil also reduces nitrogen-fixing bacteria, including *Azotobacter vinelandii* [89]. Tungsten can be taken up in considerable quantities due to its similarity with molybdenum and it may interfere with molybdenum enzymes, in which tungsten can replace molybdenum. Tungsten can deactivate some molybdenum-containing enzymes in bacteria and plants, also affecting nitrogen fixation [86,90]. Stunted root length in *Pisum sativum* and *Gossypium hirsutum* has been reported in the presence of high concentrations of tungsten [91,92].

Some species including lettuce, oats, radishes [93] growing on very polluted mine soils bioaccumulate tungsten because they have developed a tolerance towards it over time [42]. More information on the mechanisms by which tungsten in soil may influence many aspects of plant physiology, is beyond the scope of this review but is detailed in an excellent work on tungsten toxicity in plants [94].

Although tungsten seems to be absorbed quite easily by plants, little is known on how tungsten is distributed in the various parts of plants (leaves, stems, fruits), which is essential information particularly for edible species. The speciation of tungsten in lettuce plants shows the presence of both the monomeric form and the poly-tungstates. X-ray absorption spectra (XAS) and X-ray absorption near edge structure (XANES) showed that tungsten was present in lettuce as poly-tungstate in the root portion, while in the shoots it was mainly present as a monomer [95].

We must also take into account the use of the soil. Some species are able to accumulate significant quantities of tungsten, they are however grown in areas near at mining areas. Instead, it is of fundamental interest to assess the results of plants raised on agricultural soils and extend the investigations at the varietal scale to understand if different varieties of the same species have the same behavior.

A study of great interest concerned rice, which is one of the most consumed field crops, affecting over three billion people in the world. The results showed that tungsten content in the rice ranged from 0.17 mg kg^{-1} (grain) to 7.06, mg kg^{-1} (root) in plants collected in agricultural fields near tungsten mines. The authors concluded that tungsten mining contaminated the neighboring agricultural soils with a consequent increase of tungsten content in rice, which may lead to a growing health risk for inhabitants via dietary intake [45]. Similar results have been reported for brown rice cultivated in paddy soils of Southeast China. The tungsten concentration varied from 7 µg kg^{-1} to 283 µg kg^{-1}, and was significantly correlated with the available soil tungsten [96]. Recently a detailed investigation was carried out on vegetable samples of *Raphanus sativa, Spinacia oleracea, Solanum tuberosum, Nelumbo nucifera* and *Zea mays* growing in soils in the main cities in Fujian Province, Southeast China. The results showed that tungsten concentration in the vegetables was different among species. *Nelumbo nucifera* showed the lowest content (0.03 mg kg^{-1}) while *Spinacia oleracea* the highest (2.73 mg kg^{-1}) [97]. The soil properties influenced the passage of tungsten from soil to vegetables for all the species investigated. In particular, organic matter was the most important parameter that regulated the passage of tungsten in edible parts. While silt and clay amount exhibited significantly negative correlations with the translocation of the metal to shoots.

Soil–plant transfer allows the entry of tungsten into the human food chain. This underlines the importance of finding models to predict the transfer of the metal from soil to the plant. In a study with three different soils (Histosol, Fluvisol, and Vertisol), at increasing tungsten concentrations, the transfer of tungsten from the soil to corn plant was described with a Freundlich-like equation [55].

The correlation between the concentrations calculated by the model and measured in the shoots was high, with R^2 values ranging from 0.922 (Histosol) to 0.942 (Fluvisol). Similar results were obtained for the root portion with R^2 values ranging from 0.896 (Histosol) to 0.944 (Fluvisol).

The correlation is higher if the concentration of tungsten in the soil solution is considered instead of the total concentration in soil. Given the characteristics of the soils, the results from this model confirm that the uptake by plants increased from acidic soil to alkaline soils; Histosol (pH 4.50), Vertisol (pH 5.80), and Fluvisol (pH 7.40). This increase is due to the action of the alkaline pH of soil, which promoted the desorption of tungsten from soil surfaces and its release in soil solution where the metal is bioavailable for plant uptake [55]. The results are in agreement with several studies from which it appears that in acidic soil tungsten mobility is reduced [54,64,71,75].

This Freundlich-like approach is only a preliminary step in developing mechanistic models. More experiments need to be performed by varying plant species and using soils with different characteristics to improve the modeling of tungsten uptake by plants, or to develop more complex models. For example, in the case of soils subject to seasonal variations in the oxidation–reduction conditions, the redox potential needs to be analyzed [98] as it may influence the mobility of tungsten and therefore its transferability to plants.

5. The Remediation of Tungsten-Contaminated Soils

The main areas polluted by tungsten are firing ranges and mining sites. A significant cause of environmental hazard in case of tungsten mining may be also the presence of high arsenic concentrations in the tungsten deposits. Where agricultural soils are near mining sites, arsenic concentration reached about 1000 mg kg^{-1}, with impacts also on local foods (rice and vegetables) and populations [99–101]. Moreover, soil eco-toxicological studies indicate that tungsten can be toxic to invertebrates [43,102,103]. The effect has been ascribed to its action of disrupts phosphate-dependent cell signaling pathways [104].

Given the specific characteristics of these sites, the remediation technologies for tungsten are essentially the same as for other metals. Among the technologies that can be used, preliminary studies suggest that phytoremediation may be a possible technology to

clean-up tungsten-contaminated soils based on the uptake of tungsten from several plant species [55,71,86,105].

Phytoremediation is a technology that uses the natural biological processes of plants and rhizosphere microorganisms for removal or transformation of contaminants in soil. The technology is characterized by its positive impacts on the environment plus a low cost. Phytoremediation can be used both for tungsten phytoextraction and phytostabilization.

The underlying principle of phytoextraction is to use the plant as an extractant that is able to absorb metals from soil by the roots system and transfer them through the transpiration flow into the aerial part. At harvest, plants can be collected, removing the adsorbed metals from the soil. Phytostabilization involves the ability of roots to immobilize the contaminants in the root zone thus decreasing metal leaching. This technology is principally appropriate at the mining sites, where the concentration of pollutants is so high that phytoextraction would require too much time to achieve remediation targets.

The main advantages of phytoremediation are the low cost, its non-invasiveness, landscape restoration, increased activity and diversity of soil microorganisms and less human exposure to polluted substrates. The main disadvantages include the long time required for completion of the reclamation due to slow growth of the plants, the poor efficiency in contaminants removal when present at low bioavailability and the inability of the roots to reach the contaminant at considerable depths.

The full-scale application of phytotechnologies is still in a consolidation phase [106], particularly in the case of tungsten, given the complex dynamics of this metal in the soil, and the presence of polymeric forms with different levels of bioavailability. Phytoremediation is highly site-specific and it involves numerous interdependent variables (soil and its characteristics, type, concentration and depth of the contaminant, plant species, etc.).

Very positive results have been reported from laboratory studies with the use of electrokinetic remediation removal of tungsten from firing ranges soils [107]. Electrokinetic remediation (EKRT) is used for soils contaminated by heavy metals and can be successfully applied in clayey soils. By inserting electrodes into the contaminated soil, a direct current with low electric potential applied to the electrodes produces three main types of contaminant transport mechanisms [108,109]:

- Electromigration, which involves the transport of ions and other polar complexes dissolved in the pore soil solution, caused by the electrical potential applied;
- Electroosmosis, the transport of ions and dissolved contaminants due to the movement of the interstitial soil solution, generated by the presence of the electrical double layer on the charged surfaces of the solid phase;
- Electrophoresis, the movement inside the pore solution of colloidal particles with a surface charge caused by the applied electrical potential.

Metal ions are transported to the electrode with the opposite charge (electromigration). The electroosmotic flow that is produced offers a driving power for the movement of solubilized contaminants. EKRT appeared to be very efficient in removing tungsten from a contaminated soil characterized by low permeability, even in the presence of other metals, such as lead and copper. In about 75 days, more than 600 mg of tungsten were removed from the contaminated soil [107].

For sites contaminated with heavy metals, a life cycle assessment procedure highlighted that phytoremediation and EKRT are the least impacting strategies from an environmental point of view [110,111]; however, the full-scale application in the case of tungsten requires further studies in different kinds of soils and different levels of tungsten contamination.

Further means to reduce environmental impacts, saving resources and reduce costs are being studied [112,113]. Among the innovative approaches for efficient recycling of this element, microbial strategies seem to provide interesting results in the case of mining sites [114].

6. Conclusions

The aim of this overview was to generate new interest in several biogeochemical processes of W, including sorption/desorption and uptake by plants which occur in the soil environment.

To avoid environmental emergencies in the near future detailed knowledge of the behavior of tungsten is required along with its compounds in the soil.

The sustainable management of tungsten-containing materials needs a systemic approach based on the use and recycling of tungsten materials in a productive way throughout the entire life cycle of the element. The supply of tungsten could be increased by exploiting all the waste materials containing this metal. In fact, recycling hard-metal scrap could significantly reduce the cost and the environmental impact of mining on soils. In a circular economy, the huge amounts of waste produced should be considered as valuable alternative sources of tungsten.

The wide use of tungsten in numerous industrial fields including the production of clean energy highlights that this metal is indispensable to our lives. We hope that this review will contribute to further investigations into the behavior of tungsten in soil, which will also help in drawing up environmental legislations.

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