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Tungsten Bioaccessibility and Environmental Availability in Tungsten-Spiked Agricultural Soils

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Abstract: Tungsten is an essential element for many cutting-edge industries. Its use is increasing, so much that it has become a "critical element". With the increase in the use of tungsten, a possible increase in its presence in environmental matrices including soil is expected. In this research, we assessed the environmental availability and bioaccessibility of W in relation to soil properties. Four representative Mediterranean soils, collected in Italy, were spiked with tungsten and incubated for 12 months. In the spiked soils, the environmental availability of the element was determined by the Wenzel sequential extractions. The bioaccessibility was determined by the UBM (BARGE) method in both the gastric and intestinal phases. The findings indicated that the environmental availability is largely influenced by soil properties such as pH and organic matter, while a lower influence was discovered for bioaccessibility, particularly for the gastric phase. These differences could be ascribed to the characteristics of the extractants utilized in the various tests, in particular the pH values. These results could be a valuable reference to integrate with studies on really and not spiked contaminated soils, for the improvement of risk assessments and the development of strategies for remediating soils polluted with tungsten.

Keywords: environmental availability; bioaccessibility; Wenzel extraction; UBM (BARGE) method; soil properties; spiked soils

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1. Introduction

Tungsten (W) plays a vital role in various emerging key technologies, including renewable energy, energy efficiency, electronics, and various hi-tech industries [1]. Its unique properties make it indispensable for the development and optimization of various cutting-edge technologies. Rapid advances in technology have led to a growing demand for tungsten; however, its extensive use can lead to an undesirable increase in its release into the environment [2,3].

The goal of achieving the ambitious target of a CO_2-neutral society [4] will increase the pressure on the tungsten mining sector in the next years. However, as mining progresses, environmental impacts such as soil pollution can also increase. Soil contamination can occur at any stage of the life cycle of W compounds: mineral processing, production, distribution, and final disposal [2]. Therefore, W is considered as one of the emerging environmental contaminants [5].

In general, exposure to tungsten is considered very low, and to date, there are neither consistent European Union regulatory values for W in soil, nor specific reference levels in food and drinking water. Occupational exposure at higher-than-normal levels is considered only for people involved in the extraction and processing of tungsten with inhalation and dermal contact as the main exposure routes [6].

Concern regarding the health effects of tungsten first started in the USA at sites where W was suspected of being the potential cause of childhood leukemia clusters [7–10] due to the substitution of W instead of Pb in ammunition. Research on W toxicity and environmental hazards thus increased after the classification of tungsten as an emerging contaminant by the US Environmental Protection Agency in 2008 [11], with the awareness that the increasing use of W in many materials would lead to higher diffusion of tungsten in the environment, including soil. Moreover, the International Agency for Research on Cancer [12] has classified tungsten carbide, a compound used in industrial applications, as "possibly carcinogenic to humans" (Group 2B). Evidence supporting this classification is mainly based on animal studies, and the relevance to human health is not entirely clear.

In soils, tungsten occurs naturally with concentrations ranging from 0.1 to 5 mg kg^{-1} [13]; however, in certain areas, such as those adjacent to mining sites, concentrations above 1000 mg kg^{-1} have been found. In these soils, tungsten can be taken up by plants with a negative impact on the food chain [14]. Even higher concentrations of up to about 3000 mg kg^{-1} have been found in conflict zones and military firing ranges [15–17].

Only recently has there been significant interest in the behavior of tungsten in the soil, as previously it was believed to be substantially inert [15]. However, under uncertain pH conditions, soluble tungsten compounds can form in the soil [18,19]. It is thus of primary importance to establish any health risk pathways derived from its presence in the soil. Its exposure route can be indirect, from the soil to the plant and therefore to the food chain, and also direct, by ingestion of the soil. It is thus essential to consider both the environmental availability, which simulates the potential bioavailability (BAV), and the bioaccessibility (BAC) of W in soil.

Environmental availability describes the concentration of a metal in the liquid phase of the soil, and it is essential to identify the transfer of the metal from soil to plant, and thus the human exposure derived from food [20].

Bioaccessibility describes the fraction of a contaminant that is soluble in the gastrointestinal tract and which becomes available for absorption into the body [21]. Bioaccessibility needs to be considered in order to evaluate the exposure from soil ingestion which is particularly important in children deriving from the hand-to-mouth process [21].

The environmental availability of a metallic element in the soil can be determined by chemical extractions which identify the soluble or solubilizable portion [21], while bioaccessibility can be determined by in vitro tests which have replaced in vivo tests [22]. In vitro tests are based on extractions from the soil with solutions that simulate what happens in the human gastrointestinal tract. The aim is to identify how much contaminant is potentially releasable from the soil once ingested [23].

The main objective of this study was to investigate the relations between W environmental availability, bioaccessibility, and soil characteristics. The findings could provide useful preliminary information, even if there is no in vivo validation for this element for health risk assessments in W-contaminated soils in light of its increasing use in daily life. Tungsten pollution is often considered in sites with very high concentrations such as mining sites [24]. However, its increasing use in many products for daily use means that the possible environmental effects of much lower concentrations than those found in the vicinity of mining sites need to be assessed, particularly as the levels are much higher than the current background values of non-contaminated soils.

For this purpose, following an approach frequently tested with other metallic elements, such as Hg [25], Mo [26], Cd, and As [27,28], soils of different origins were spiked to simulate a high soil concentration of 50 mg kg^{-1}. This value is very high for natural soils, but much lower than concentrations found in, or nearby, mines [14,29,30].

2. Materials and Methods

2.1. Soil Characterization and Spiking

We collected four surface soils in Italy which are characteristic of the Mediterranean area. According to the FAO classification, the soils were defined as Entisol, Cambisol, Vertisol, and Histosol, respectively. Soils were air-dried, sieved to 2 mm, and spiked with tungstate (sodium tungstate, Sigma-Aldrich, St. Louis, Mo, USA) which is the main chemical form in the soil under oxidizing conditions. The spiked soils were maintained at

70% water holding capacity and incubated for 12 months at 25 °C. The soils were mixed by hand and, if necessary, the moisture content was adjusted every month during the incubation period [31]. The experiments were carried out in triplicate.

The soils were spiked to obtain a final concentration of 50 mg kg^{-1} of tungsten in each of the soil samples. This concentration, which is very high for unpolluted soils, was selected on the basis of the Igeo index [32–34].

$$\text{Igeo} = \text{Log}_2\left(\frac{\text{Cm}}{1.5 \times \text{Rm}}\right), \quad (1)$$

where Cm represents the concentration of W in spiked soil and Rm is the original value in soils which is considered the reference value for tungsten, and the constant 1.5 is applied to eliminate lithological fluctuations [35].

Considering the original W concentration in the soils (about 0.30 mg kg^{-1}) as the background value, we selected a final concentration of tungsten that would lead to an Igeo value of around 7, which is characteristic of highly contaminated soils [36].

2.2. Tungsten Environmental Availability and Bioaccessibility Evaluation

Analyses of soil properties (pH, organic matter, cation exchange capacity, clay, silt, and sand) and W environmental availability were performed on the 2 mm air-dried soil fraction by standard methods [37]. To evaluate W environmental availability (BAV) the Wenzel sequential extraction procedure (SEP) [38] was used as it is considered the most appropriate for tungsten speciation [39].

The five fractions of the Wenzel SEP were determined using the following extractions: F1: 0.05 M $(NH_4)_2SO_4$, 4 h, 25 °C ratio soil/extractant 1:25; F2: 0.05 M $NH_4H_2PO_4$, 16 h, 25 °C ratio soil/extractant 1:25; F3: 0.2 M NH_4-oxalate buffer in the dark (pH = 3.25), 4 h, 25 °C ratio soil/extractant 1:25; F4: 0.2 M NH_4-oxalate buffer + 0.1 M ascorbic (pH = 3.25), 0.5 h, 96 °C ratio soil/extractant 1:25; and F5: HNO_3–$HClO_4$, 180 °C ratio soil/extractant 1:50 [39]. Tungsten recovery by this method ranged from 98.8% to 101%.

W bioaccessibility was determined in the soil fraction <250 nm particle size according to the unified BARGE method (UBM) prepared and validated by the Bio Accessibility Research Group of Europe (BARGE) [40]. Bioaccessibility is evaluated in the soil fraction of <250 mm, since this is the one that tends to adhere to children's hands and can be ingested through the subsequent passage from the hands to the mouth [27,41–43]. The UBM method, which is also the basis of the ISO 17924:2018 method [44] to test soil quality, has been validated in vivo for the bioaccessibility of arsenic, cadmium, and lead in soils [45]. In vitro testing avoids using animal experiments, is rapid, and has a low cost. The UBM method differentiates between a gastric phase (GP) and a gastrointestinal phase (IP). In the GP, the sample is exposed to a simulated gastric fluid that mimics the acidic and enzyme-rich environment of the stomach at a pH of the solution adjusted to 1.2 ± 0.05. This stage identifies the gastric bioaccessibility (BACg). In the IP, the sample is exposed to a simulated intestinal fluid that replicates the alkaline and enzyme-rich environment of the small intestine at a pH ranging from 5.8 to 6.8. This stage identifies the intestinal bioaccessibility (BACi).

The quantitative health risk assessment of exposure to W In soils due to oral ingestion for adults and children was evaluated by the USEPA procedure [46,47]. The daily intake (CDI, mg kg^{-1} day^{-1}) of W through incidental ingestion of soil was calculated using the following Formula (2):

$$\text{CDI} = \frac{\text{C} \times \text{IR} \times \text{EF} \times \text{ED} \times 10^{-6}}{\text{BW} \times \text{AT}} \quad (2)$$

where C is the W total concentration in soil (mg kg^{-1}), IR is the soil ingestion (mg day^{-1}, 100 for adult and 200 for children), EF is the exposure frequency (day $year^{-1}$, 250), ED is the exposure duration (25 years for adults and 6 years for children), BW is the body weight (80 kg for adults and 15 kg for children), and AT is the average time of exposure (AT = ED × 365 days) [46].

The non-cancer risks can be derived by the hazard quotients (HQ) defined by the equation [47]:

$$HQ = \frac{CDI}{RfD} \times BAC \tag{3}$$

where RfD is the oral reference dose corresponding to W and is 0.0008 mg kg^{-1} day^{-1} [24], and BAC is the bioaccessibility expressed as a percentage of the total concentration [48]. It must be underlined that the Equation (3) should be considered approximate. The true equation should take into account the relative bioavailability instead of absolute bioaccessibility.

2.3. Tungsten Analysis

Tungsten concentrations in the supernatants of the sequential extraction (SEP), BACg, and BACi phases were measured by inductively coupled plasma optical emission spectroscopy (ICPOES Varian AX Liberty Varian, Milan, Italy). Operating parameters: wavelength 239.709 nm, plasma flow = 16.5 L·min^{-1}, auxiliary flow = 2.25 L·min^{-1}. The original W concentration in the soils was determined including the standard enrichment procedure by the USEPA method 3050B using the specific digestion procedure with the addition of phosphoric acid to nitric acid established by Dermatas et al. [49] and reported by Bednar et al. [50]. All chemicals used were of reagent grade.

2.4. Quality Assurance and Quality Control

Quality assurance and quality control were performed using a certified reference soil material (NIST SRM 2710), testing a standard solution every 10 samples as well as at the end of the analytical sequences. The W limit of quantification (LOQ) was 0.05 mg·L^{-1}. The recovery of spiked samples ranged from 95% to 102%, with an RSD of 1.86 of the mean. All experiments were performed in triplicate.

2.5. Statistical Analysis

Data are reported as the mean of three replicates ± standard deviation (±SD). Statistical analysis was executed by STATISTICA v. 6.0 (Statsoft, Inc., Tulsa, OK, USA).

3. Results and Discussion

The characteristics of the four soils are reported in Table 1. Soil pH ranged from acid (4.7) to strong alkaline (8.1). Soil textures varied from loamy to sandy loam and organic matter ranged from 1.08 to 5.32%. The characteristics of the soils remained unchanged after spiking.

Table 1. Selected properties, means (n = 3), and standard deviations (SD, in brackets) of the soils used.

Soil Classification	Entisol	Cambisol	Vertisol	Histosol
Textural class	Sandy loam	Loamy	Loamy	Sandy loam
pH	6.2 (0.02)	7.3 (0.04)	8.1 (0.03)	4.7 (0.03)
Organic matter%	3.1 (0.33)	1.08 (0.22)	1.1 (0.27)	5.32 (0.48)
C.E.C (cmol (+) kg^{-1})	21.4 (1.4)	10,6 (0.7)	16.2 (0.8)	25.6 (1.1)
Clay%	15.6 (0.4)	13.3 (0.7)	23 (1.1)	10.4 (1.0)
Silt%	26.6 (0.5)	46.4 (0.9)	42 (0.7)	23.6 (0.9)
Sand%	57.8 (0.5)	40.3 (1.2)	35 (1.0)	66.0 (1.4)
Total W mg kg^{-1}	0.25 (0.4)	0.36 (0.4)	0.29 (0.4)	0.32 (0.4)
Fe%	2.8 (0.17)	3.1 (0.11)	2.4 (0.16)	4.2 (0.15)

3.1. Environmental Availability

Wenzel sequential extraction is a widely used procedure for determining the distribution of anions such as arsenate in various environmental samples [38], and it has also been recommended for tungstate in soils [39]. The selective chemical extractions that mimic different environmental conditions operationally separate specific forms of tungsten. The purpose of this SEP was to assess the potential mobility and environmental availability of

W in the soil environment. The extractability of W assessed by the Wenzel SEP is reported in Table 2.

Table 2. W concentrations in the fractions of Wenzel SEP in the four soils investigated. The data means (n = 3) and standard deviations (SD, in brackets) are expressed as mg kg^{-1} on a dry weight basis for each fraction.

Fractions	Entisol	Cambisol	Vertisol	Histosol
F1	0.25 (0.05)	0.55 (0.04)	0.75 (0.05)	0.15 (0.04)
F2	1.60 (0.4)	2.42 (0.6)	2.53 (0.5)	1.05 (0.1)
F3	7.51 (0.5)	6.53 (0.3)	5.52 (0.3)	4.51 (0.2)
F4	16.0 (1.2)	14.0 (1.1)	11.5 (1.2)	8.50 (1.0)
F5	24.6 (1.8)	26.5 (1.7)	29.7 (1.8)	35.9 (1.9)

According to the Wenzel scheme, the following fractions were operationally defined as follows:

F1, non-specifically sorbed (easily mobilizable, outer-sphere complexes); F2, specifically-sorbed (readily mobilizable, inner-sphere complexes); F3, bound to amorphous and poorly-crystalline oxides; F4, bound to well-crystallized hydrous oxides; and F5, residual. The first step (F1) involved the extraction of tungsten that was loosely bound to the sample's surface through ion exchange or non-specific adsorption processes, since a weak electrolyte, such as ammonium sulfate, was used. Tungsten in this fraction was considered relatively mobile and in bioavailable chemical forms, which can be easily released into the environment. This fraction is thus very important in determining environmental risks. In this specific case, in the four soils examined, the fraction F1 ranged from 0.3 (Histosol) to 1.5% (Vertisol).

As regards fraction F2, the extraction was performed using phosphate ion. The exchange between phosphate and tungstate thus suggests that tungstate can form inner-sphere complexes with inorganic soil colloids [51]. The percentage obtained varied from 2.1% (Histosol) to 5.0% (Vertisol).

Fraction F3 contained tungsten linked mainly with iron oxides/hydroxides. This fraction was extracted using ammonium oxalate buffer, which is a stronger reagent extracting the metal associated with amorphous oxides. Tungsten associated with oxides is considered to have low mobility under most environmental conditions. The percentages of tungsten in this fraction were significant and higher than the sum of F1 and F2, ranging from 9% (Histosol) to 15% (Entisol).

The tungsten determined in fraction F4 was linked to the crystalline oxides/hydroxides of iron. The addition of ascorbic acid in the buffer solution increased the reductive potential of the extractant to efficiently target the crystalline oxides. The percentages of tungsten in this fraction ranged from 17% (Histosol) to 32% (Entisol) of the total content in the soil.

Fraction F5, in which W was in residual tightly bound forms, reached quite high percentages from approximately 50% to 70%. The residual fraction F5 was generally the highest in aged W-contaminated soils [39], and also in the case of W-spiked soils [31]. In the latter case, and also in our experiments, the high W concentrations in this fraction can be ascribed to the strong linkage of W with soil solid phases, notwithstanding the lack of immobilization in soils during aging [31].

The distribution of tungsten in the soil was in the following order: residue (F5) > crystalline iron and aluminum oxides/hydroxides (F4) > iron and aluminum oxides/hydroxides (F3) > specifically adsorbed tungsten (F2) > exchangeable chemical forms (F1). These results, which can be ascribed to the affinity of W for more stable soil phases, are similar to those found for other oxyanions such as arsenic [39].

The Wenzel SEP can be used to evaluate the risk linked with soil contamination. Anions, such as arsenic, have been defined by the so-called mobility factor (MF%) which takes into account only the concentration of an element in the F1 fraction with respect to the total concentration in soil [52–54]. However, a better evaluation of the most mobile amount of W can be obtained by defining a potential environmental availability ($BAV_p\%$) according to Equation (4).

$$BAV_p\% = \frac{F1 + F2}{W_{tot}} \times 100 \quad (4)$$

This parameter ($BAV_p\%$) takes into account the fact that the bioavailable amount of W with respect to the total (W_{tot}) is not only defined by fraction F1 characterized by non-specific adsorption, but also by fraction F2 in which $NH_4H_2PO_4$, an extractant that solubilizes W forms involved in specific adsorption, is used [55]. Especially in agricultural soils, where phosphatic fertilizers are very commonly used, the presence of phosphate can promote the release of W compounds from the solid phase, due to the phosphate–tungstate exchange competition [56]. Figure 1 compares the index MF% and $BAV_p\%$.

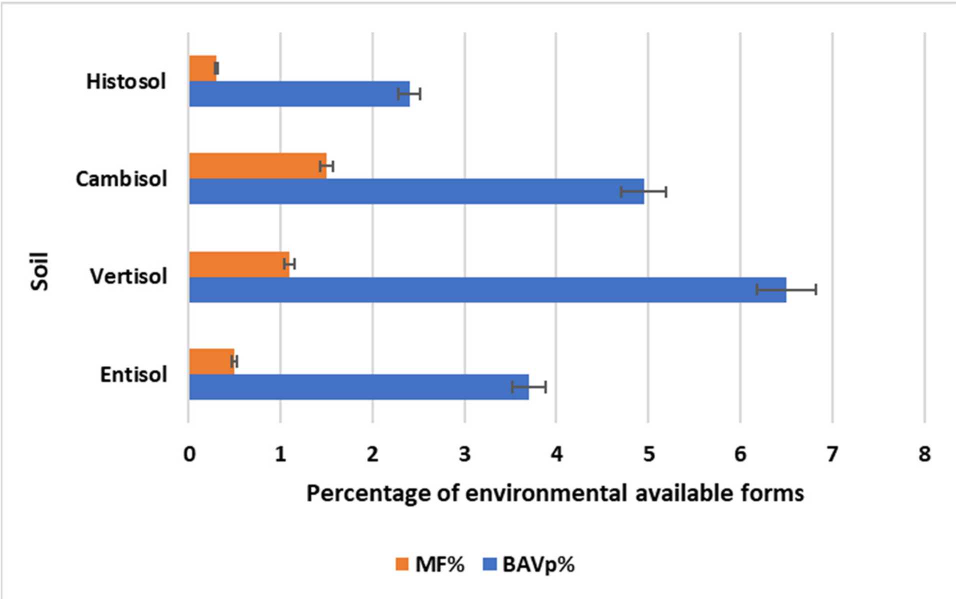

Figure 1. Environmental availability determined by mobility factor (MF%) and potential environmental availability ($BAV_p\%$). Values are the means of three replicates and the error bars show the standard deviations.

The results obtained showed that the mean $BAV_p\%$ ranged from 2.4% (Histosol) to 6.5% (Vertisol), suggesting the not negligible environmental availability of W in the studied soils. This is in agreement with the findings of previous works in which a significant transfer of W from the soil to the plants has been reported [31,57,58]. The use of the BAVp% can be considered more precautionary than MF% in assessing the risk derived from the transfer of tungsten from the soil to the plant and therefore to the food chain.

Potential environmental availability is linked to the characteristics of the soils used and is generally positively correlated with the pH of the soils (R^2 = 0.977) and inversely with the organic matter content (R^2 = 0.956). On the other hand, the Fe content seems to have less influence on this quantity, as can be seen from the correlation (R^2 = 0.649). The correlation with clay is even lower (R^2 = 0.553). Data are reported in Table 3.

Table 3. The linear regressions of tungsten potential environmental availability (BAVp) against soil characteristics.

Soil Properties	Equation	R^2
pH	BAV_p = 1.441 pH + 3.26	0.977
OM	BAV_p = −1.950 OM + 7.13	0.955
Clay	BAV_p = 3.962 Clay + 6.46	0.552
Fe	BAV_p = −0.615 Fe + 4.53	0.649

3.2. Bioaccessibility

Considering the quantity of a metallic contaminant as totally bioaccessible is too conservative and can lead to the incorrect assessment of the risk derived from the ingestion of soil [59]. The UBM method mimics the release of W from soil subsequently to the passage through the mouth, stomach, and small intestine [44,45,60–62]. The method has also been successfully used for different metals and also to investigate the bioaccessibility of molybdenum, the companion element of tungsten [26]. Table 4 reports the concentrations of bioaccessible W in simulated gastric (BACg) and intestinal (BACi) phases for all the soils investigated in the present study. The values obtained are very high probably due to spiking of soils.

Table 4. Tungsten concentrations in BACg and BACi in the four investigated soils. Data (mg kg^{-1}) are reported as means (n = 3) and standard deviations (SD, in brackets).

Soil	BACg	BACi
Entisol	19.1 (0.21)	20.1 (0.51)
Cambisol	15.6 (0.11)	19.3 (0.32)
Vertisol	14.8 (0.09)	20.8 (0.50)
Histosol	13.2 (0.09)	14.0 (0.10)

Bioaccessibility is commonly expressed as a percentage, considering the ratio between the bioaccessible concentration of the contaminant BACg or BACi and the total W concentration in the soil sample.

Bioaccessibility expressed as a percentage is reported in Figure 2. BACg% was higher in Entisol with a percentage value of 38.1%. The lowest value was found in Histosol with an extractability percentage of 26.4%. The BACi% was still the lowest in the case of Histosol (28.1%), but the highest for Vertisol, reaching 41.6%. However, this value is very similar to the percentage in Entisol (40.2%) and Cambisol (38.6%). A significant amount of the total W content was not available for absorption in the gastrointestinal tract following soil ingestion. This is in agreement with results on tungsten in ore-processing residue (TOPR) [63] and for other anions such as Mo and As, in different soils [26,64].

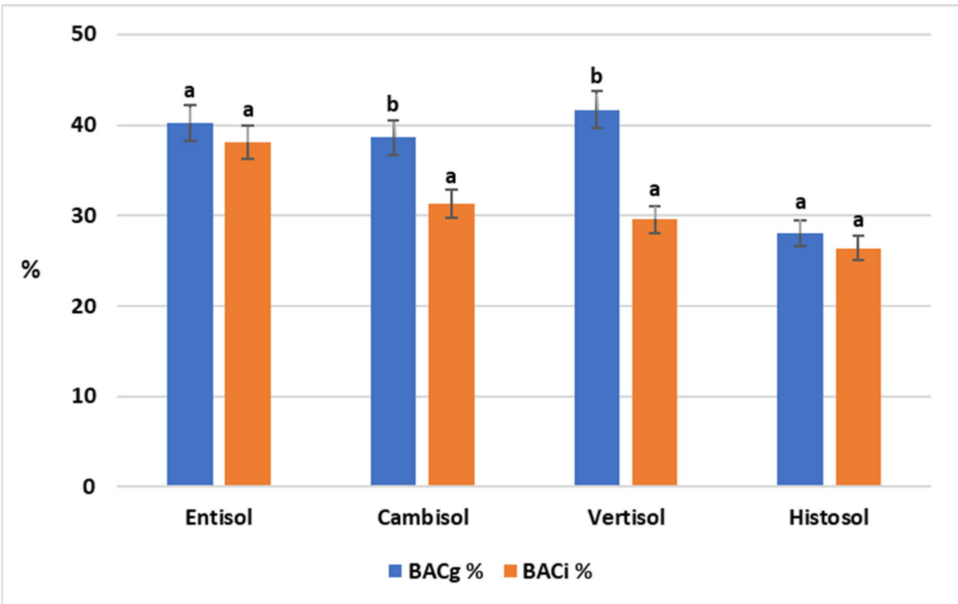

Figure 2. Bioaccessibility (BACg and BACi) percentage in the four investigated soils. Values are the means of three replicates and the error bars show the standard deviations. Values with different letters are significantly different at the 5% probability level (Tukey's test).

The figure shows that there are no large differences between the two fractions BACg and BACi, although the BACg fraction is slightly higher than the BACi. The results of the soils investigated in this study are in agreement with findings in a recent article on the bioaccessibility of W, determined on TOPR, a very different environmental matrix from soil [63]. However, the data do not reflect the findings obtained regarding the bioaccessibility of molybdenum in other soils of a different nature [26].

We observed different correlations between W bioaccessibility and soil properties such as pH, clay content, OM, and Fe content in soils. Considering these soil characteristics, BACg was not found to be correlated with soil properties such as pH (R^2 = 0.034), OM (R^2 = 0.061), and clay (R^2 = 0.026), and also the correlation with Fe content (R^2 = 0.298) was very low. The very acidic value of the extractant used in the UBM method for the gastric phase probably drastically lowered the effects derived from the characteristics of the four different soils because it solubilizes a considerable quantity of W. In addition, the W adsorbed on the iron oxides is released because the oxides are solubilized at acidic pH.

In contrast, BACi appeared to be related to the soil characteristics: pH (R^2 = 0.764), OM (R2 = 0.742), clay (R^2 = 0.603), and Fe (R^2 = 0.969). Data are reported in Table 5.

Table 5. The linear regressions of tungsten bioaccessibility (BACg and BACi) against soil characteristics.

Soil Properties	Equation	R^2
pH	BACg = 0.311 pH + 13.63	0.0344
	BACi = 1.830 pH + 6.54	0.7644
OM	BACg = −0.303 OM + 16.48	0.0612
	BACi = −1.317 OM + 22.06	0.742
Clay	BACg = 0.0741 Clay + 14.52	0.0261
	BACi = 0.444 Clay + 11.65	0.603
Fe	BACg = −1.747 Fe + 21.13	0.298
	BACi = −3.931 Fe + 30.86	0.969

In the test to assess the gastro-intestinal phase, the increase in pH from very acidic values to those characteristics of the soil environment (pH about 6.0) caused the amount of W extracted to be related to the soil properties. Similar results were obtained for other oxyanions, such as arsenate [65] and molybdate [26]. The key role of soil pH in metal bioaccessibility found in our study is in agreement with results obtained with different soils and different metals [34,36], also due to its influence on the surface charge Fe oxides [66].

Soil organic matter has been reported to influence the bioaccessibility of anions by complex and simultaneous reactions involved in the adsorption processes [23,26]. Organic matter is considered one of the most important factors also in W adsorption in soil as it reduces the amount of the metal in the soil solution [2,67,68]. In fact, our data confirm that the Histosol characterized by the highest OM content showed the lowest BACi, in accordance with results obtained for other oxyanions [27,28,69].

Clay showed the lowest influence on bioaccessibility, in line with data reported on arsenate [27,70,71], and probably due to the relatively lower influence of clay on the W adsorption capacity of soils [2,67].

The high correlation between BACi and Fe content in soils could be due to the adsorption processes of W on Fe oxides/hydroxides. Fe oxides/hydroxides, which are characterized by a high specific surface area and high porosity, may retain W in the internal pore network, thus reducing W solubility. Histosol, with the highest Fe content, thus showed the lowest bioaccessibility. Similar results have been reported for arsenate bioaccessibility [72].

Recent studies on the assessment of human health risks due to soil metal pollution have begun to develop models incorporating bioaccessibility [48,73–76]. It has been recognized that total content-based assessment leads to an inaccurate identification and overestimation of the health risk [74].

The health risk assessment of the four tungsten-spiked soils was performed according to the US EPA method [47] regarding contaminated sites. The quantitative risk assessment from oral ingestion was determined by calculating hazard quotients (HQ) considering 50 mg kg^{-1} soil as the exposure concentration. Taking into consideration that the soil ingestion pathway is particularly important for children, the HQ was calculated both for adults and children. The data are reported in Figure 3.

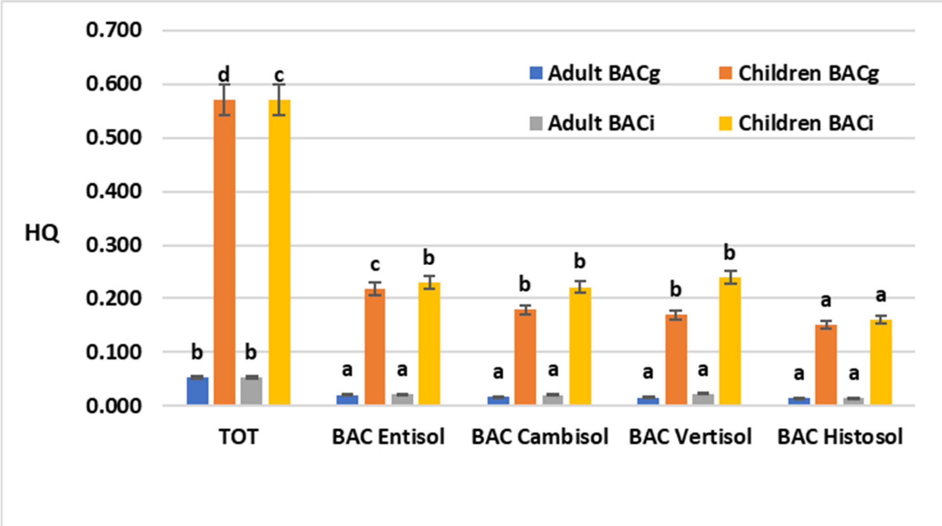

Figure 3. Hazard quotient (HQ) for adults and children based on total W content (TOT) or considering W bioaccessibility (BAC) of investigated soils. Values are the means of three replicates and the error bars show the standard deviations. Comparison of HQ is among bars with the same colours. Values with different letters are significantly different at the 5% probability level (Tukey's test).

The results showed that the bioaccessibility was not very different between the four soils investigated. All the soils were below the acceptable risk level (HQ < 1); thus, the level of concentration used can be considered as safe. In addition, if we consider the bioaccessible W instead of the total, the HQ value decreases further. However, these data should not lead to underestimating the possible dangers derived from high concentrations of tungsten in the soil. In fact, the toxicity of some compounds of W is being investigated by the International Agency for Research on Cancer [12]. Several studies have also shown the link between W and some human diseases and a potential association with leukemia [19]. Figure 3 also shows that the value of HQ is much higher considering children. This highlights the importance of the intended use of the soil, because, in the case of public parks, children are the most exposed category. Note that in this study, the focus was exclusively on tungsten; however, tungsten can often amplify the effects of other co-exposures, which could cause greater toxicity or more severe disease [77].

Food ingestion also influences W bioaccessibility, due to the presence of compounds such as proteins and low-molecular-weight organic acids, which can increase or decrease the solubility of the element in the gastrointestinal phases [63,78,79].

3.3. Environmental Availability and Bioaccessibility

Environmental availability and bioaccessibility which identify two different risk pathways provide important information for evaluating the potential transfer of W from soil to humans. The results obtained show that these two parameters may be to a greater or lesser extent influenced by soil characteristics.

Considering the environmental availability of tungsten expressed by the tungsten potential environmental availability BAVp% and the bioaccessibility defined by BACg% and BACi%, a notable difference can be seen between the three quantities (Figure 4).

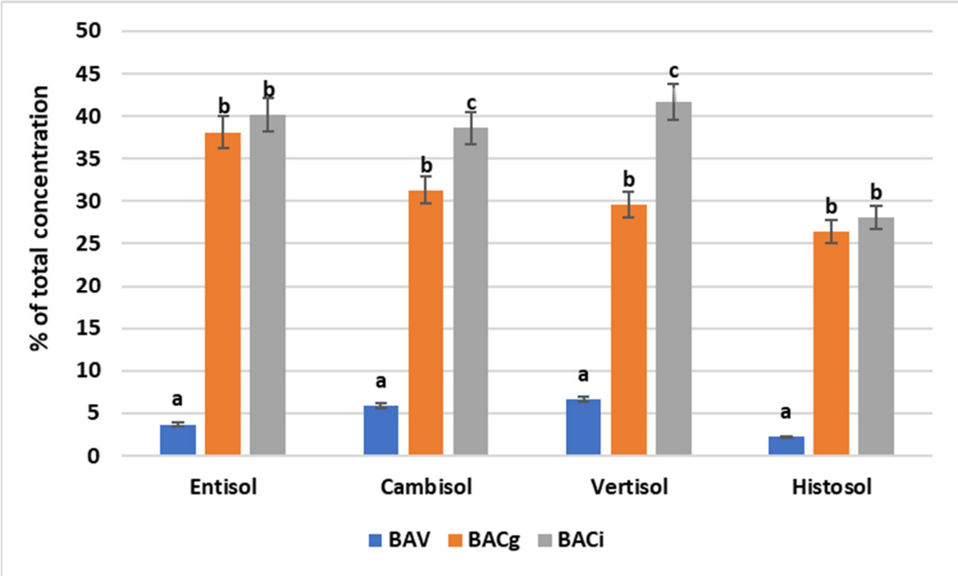

Figure 4. Environmental availability and bioaccessibility, expressed as percentages (BAV_p%, BACg%, and BACi%) of the total W concentration in the investigated soils. Values are the means of three replicates and the error bars show the standard deviations. Values with different letters are significantly different at the 5% probability level (Tukey's test).

Figure 4 highlights how the quantity of environmentally available tungsten is much lower than that of bioaccessible tungsten. Furthermore, no correlation was detected between the concentration of available W determined by the Wenzel extraction and the bioaccessible W in the gastric phase (BACg). A similar lack of correlation was also reported by Luo et al. [73]. However, considering the intestinal phase, BACi appears to be linked to the properties of the soil, which also determine the environmental availability of the tungsten. The different trends in environmental availability and bioaccessibility in the soils could be explained by the different chemical compositions and thus be due to the different actions of the extractants used to determine BAV_p, BACg, and BACi. A comprehensive human health risk assessment is therefore necessary, combining bioaccessibility and environmental availability, with careful attention paid both to the kind of extractant solutions and the characteristics of the compounds investigated.

The association between environmental availability and bioaccessibility in a monitoring strategy should include the aspect of time, and further work is needed to provide estimates of both the immediate and potentially available or accessible fractions. Both the environmental availability and bioaccessibility of tungsten can change over time due to modifications in soil parameters such as pH, organic matter content, and changes in land use. In fact, soil spiked experiments have some limitations due to the lack of aging processes, which also influence the chemical form of the contaminants [80,81].

4. Conclusions

There is a growing concern regarding the possible adverse effects on human health caused by increasing levels of tungsten in the environment. An assessment of the environmental availability and bioaccessibility is thus essential to determine whether the W concentration that is present in the soil could have negative effects on humans and the environment.

Although our study on four soils cannot be generalized to all soils, the results highlight that soil characteristics are critical in determining the environmental availability of tungsten, while bioaccessibility is less influenced by the soil properties as shown by the BACg values. The fact that bioaccessibility does not strictly depend on the characteristics of the soils studied suggests that increasing the concentration in the soil could correspond to an increase in the bioaccessible fraction, as some soil characteristics seem unable to effectively retain the metal in the solid phase. This is particularly significant for the assessment of risks to the health of children because of the hand-to-mouth pathway. The combination of environmentally available fractions of soil, which influence the transfer of the metal to the food chain, and bioaccessible fractions involved in the oral ingestion pathway could also be used to define the limits to tungsten in regulations concerning soil, which currently do not account for tungsten.

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