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Influence of Arsenate Competition on Tungstate Sorption by Soil

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Abstract: The green and digital transitions toward sustainable development will drive an increased demand for critical raw materials, among which tungsten plays a crucial role in emerging sustainable technologies. Understanding the sorption processes of tungsten in soils is essential for assessing its bioavailability and potential toxicity to living organisms. In many soils, tungsten may co-exist with other contaminants, such as arsenic. Investigating the competitive sorption between these two anions helps clarify how they interact within the soil matrix. Batch experiments were conducted on three Mediterranean soils to evaluate the sorption behavior of tungstate and arsenate, both individually and in combination, using a "Langmuir-type" model. Both anions exhibited the highest sorption in acidic soils and the lowest in alkaline soils. While the shapes of the isotherms were similar in both single and binary systems, the maximum sorption values decreased when a co-occurring anion was present. These reductions can be attributed to competition for soil sorption sites, which have a high affinity for both anions. In all tested soils, the percentage decrease in arsenate sorption in the presence of tungstate was greater than the decrease observed for tungstate in the presence of arsenate. Gaining a deeper understanding of tungsten's sorption mechanisms is critical, not only for advancing environmental research but also for informing regulations that currently give limited attention to the presence of tungsten in soils.

Keywords: tungsten sorption; binary system sorption; Mediterranean soils; Langmuir-type model

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1. Introduction

The green and digital transitions toward sustainable development are driving an increased demand for critical raw materials. Among these, tungsten (W) plays a crucial part in sustainable industrial activities, such as renewable energy production and efficiency, electronics, and high-tech manufacturing [1–3]. Due to its exceptional characteristics, tungsten is essential for the advancement of these innovative technologies [4]. However, the rapid technological development has led to a growing demand for tungsten, which could result in increased environmental release [5].

While W is mainly of geogenic origin in soils, industrial activities involving tungsten processing or the use of tungsten-containing products also contribute to its environmental release. Soil concentrations of tungsten typically range from 0.5 to 80 mg/kg, with surface layers often exhibiting lower levels, between 0.2 and 5 mg/kg. Additional sources of tungsten contamination in soil include industrial discharges, military operations, atmospheric emissions, and improper waste disposal [4,6–8].

The toxicological profile of tungsten remains incomplete, yet it is no longer regarded as inert, as was previously assumed [9]. Recent research has identified adverse influences on human health and the environment [10–12]. Interest in tungsten surged following instances of leukemia in the USA, which were linked to environmental W contamination [13,14]. The implications for human health are particularly concerning [15], especially given the rising utilization of the element in military products [16]. Tungsten is now employed as a replacement for lead in weapons and as a substitute for depleted uranium in various

military technologies [17]. Tungsten was flagged as a potential health hazard in 2016 and subsequently listed on the EPA National Priorities List [18].

Under certain conditions, such as high soil pH, the element can become soluble and migrate through the soil into groundwater [19,20]. There is also potential for tungsten to bioaccumulate in the food chain, as plants can absorb significant amounts of tungstate depending on soil properties [21–23]. Therefore, understanding the dynamics of tungsten in soil is crucial for developing appropriate environmental regulations, which currently do not fully address this element.

The behavior of tungsten compounds in soil is largely governed by sorption processes [6]. Research has primarily focused on sorption involving soil components such as clays [24] and metal oxi-hydroxides [25–28]. Understanding these sorption processes is essential for assessing the bioavailability and potential toxicity of tungsten to living organisms, including humans. Tungsten entering the soil typically binds to the solid phase via sorption, both on the mineral and the organic matrix. The strength and type of sorption determine the first step of the bioavailability processes, i.e., the release of tungsten from the solid phase, where it remains largely inaccessible, into the liquid phase, where, in the form of tungstate, it becomes more readily available to organisms. High concentrations of tungsten in soil can be toxic to plants and organisms by reducing plant and soil microbial growth. In addition, the element can create reproductive toxicity problems for earthworms [8].

In some cases, other contaminants, such as arsenic (As), coexist with tungsten, leading to overlapping contamination in areas affected by tungsten mining activities. This can result in soil contamination by both metals [29–31]. Arsenic is naturally present in uncontaminated soils but can also be introduced into agricultural environments through the use of sewage sludge, arsenic-containing pesticides, and certain phosphates that may contain this metal [32]. The negative effects of arsenic, including inhibition of plant photosynthesis and growth and numerous health problems to soil macro- and microorganisms, are very diffuse. The element is considered one of the most important contaminants of the natural and anthropic ecosystems [32].

Significant differences exist in the chemical properties and reactivity of tungsten and arsenic due to their intrinsic characteristics and interactions with environmental components. However, tungstate (WO_4^{2-}) and arsenate (AsO_4^{3-}), the most common anion species in aerated soils, are chemically similar and can interact in processes such as sorption, ion exchange, and other chemical reactions in the environment [33,34]. Furthermore, the presence of arsenic has been reported to influence the microbial community in tungsten-rich soils [35,36].

In recent years, there has been increasing interest in the sorption of tungsten onto various matrices. However, few studies have addressed the competitive sorption of tungstate with other anions in real soils rather than specific soil components [37]. Investigating competitive sorption can help clarify how these two anions interact in soil, thereby contributing to a better understanding of the risks associated with environmental pollution. Additionally, insights into competitive sorption in soil can provide valuable information for developing sustainable remediation technologies to remove these elements from the environment.

The aims of this research were to evaluate the effect of arsenic competition on tungsten sorption in three agricultural soils typical of Mediterranean regions, each with distinct physical and chemical properties. Arsenic contamination is one of the most significant environmental hazards worldwide [38,39], and the sorption of arsenic compounds has been extensively studied over the past 30 years. Therefore, in this study, we did not delve deeply into this topic, instead referring to numerous specific articles and comprehensive reviews [40–42]. This study focused on tungsten and its interaction with arsenic, recognizing that multiple elements may coexist in certain environmental conditions, not only in mining areas [8,43,44] but also in soils naturally containing arsenic from both natural and anthropogenic sources.

In this article, the term "sorption" is used to encompass all phenomena contributing to the transfer of studied anions from the soil liquid phase to the soil solid phase [45].

2. Materials and Methods

2.1. Soil Characterization

The experiments were conducted on three Mediterranean soil types, Histosol (H), Cambisol (C), and Vertisol (V), in accordance with the soil FAO classification. These soils were characterized by a very low tungsten (W) concentration (approximately 0.30 mg/kg), among the lowest found in Italian soils. Arsenic (As) levels in Italian soils are highly variable, ranging from 10 to 40 mg/kg in some regions, primarily due to natural factors, although cases of anthropogenic contamination have also been reported. For this study, soils with arsenic concentrations typical of uncontaminated soils, lower than 8 mg/kg, were selected.

The soil samples were air-dried and sieved to ensure they passed through a 2 mm mesh for property analysis. Soil pH (using a 1:2.5 soil-to-water ratio), organic matter (OM), and cation exchange capacity (CEC) were assessed following the guidelines in the Chemical Methods of Soil Analysis by the Soil Science Society of America [46]. Particle size distribution was evaluated based on the Physical Methods of Soil Analysis provided by the same organization [47].

2.2. Sorption Experiments

The sorption tests were conducted by evaluating the behavior of tungsten and arsenic individually (single system) and in combination (binary system). For both systems, 1 g of soil sample was mixed with 25 mL of solution containing increasing concentrations of sodium tungstate ($Na_2WO_4 \cdot H_2O$) or sodium arsenate (Na_2AsO_4) ranging from 0.2 to 2.5 mmol/L in 60 mL polypropylene centrifuge tubes. In the binary system, the conditions were identical to those in the single system, but the 25 mL of tungstate (or arsenate) solution added to 1 g of soil contained fixed concentrations of the competing anion (As or W) at 1.5, 2.0, and 2.5 mmol/L. The addition of the competing ion was carried out at different concentrations to obtain an adequate range of soil surface coverage of both anions.

A background electrolyte of 0.01 M NaCl was used to maintain constant ionic strength. Sorption isotherms of tungstate and arsenate were carried out under the same experimental conditions in both single and binary systems. Different contact times were tested using the highest initial (tungstate or arsenate) concentration of 2.5 mmol/L to determine the optimal equilibration time. Results indicate that, for both the single and binary sorption processes, equilibrium was reached approximately at 18 h. Thus, solutions of the sorbate (W or As) were added to 1 g of soil and stirred at 288 K for 18 h. Suspensions were then centrifuged at 9500 rpm for 15 min, and the clear liquid supernatant was filtered through 0.2 µm Whatman filter paper for the analysis of W and As. All the sorption experiments were carried out in triplicate.

The quantity of tungstate or arsenate sorbed per unit mass of soil was determined by the difference between the quantity added and that recovered in the equilibrium solution, according to the equation,

$$q = \frac{[V * (C_i - C_e)]}{m}, \quad (1)$$

where q = the amount of anion sorbed per unit mass of soil (mmol/kg), C_i = the initial anion concentration (mmol/L), C_e = the anion concentration at equilibrium (mmol/L), V = the volume solution added (mL) containing tungstate or arsenate, and m = the mass of soil used (g).

2.3. Tungsten and Arsenic Analysis

Tungsten concentration in the supernatants of the sorption experiments was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian AX Liberty, Varian, Milan, Italy). The original tungsten concentration in the soils was determined following the USEPA method 3050B, with a modified digestion procedure that

includes the addition of phosphoric acid to nitric acid, as developed by Dermatas et al. [48] and described by Bednar et al. [49]. Arsenic analysis was performed by ICP-OES (Varian AX Liberty) using a hydride generation method [46]. All chemicals used were of reagent grade.

2.4. Quality Assurance and Quality Control

For W, NIST SRM 2710 was employed as certified soil. W detection limit was 0.02 mg/L. Spiked solutions showed a recovery range from 94% to 100% with an RSD of 1.89%.

For arsenic, the reference material CRM ERM—CC141 was used, yielding values of 7.3 ± 0.9 mg/kg, closely matching the certified values of 7.5 ± 1.4 mg/kg. The detection limit for arsenic was determined to be 50 µg/L. Spiked samples (5%) showed a recovery rate between 92% and 101%, with an RSD of 1.90%.

2.5. Statistical Analysis

Results are presented as the average of three replicates ± standard deviation (SD). Statistical assessments were carried out using STATISTICA v. 6.0 (Statsoft, Inc., Tulsa, OK, USA).

3. Results

Table 1 outlines the characteristics of the three soils. Soil pH varied from acidic (4.7) to alkaline (8.1). Soil textures ranged from loamy to sandy loam, while organic matter content varied between 1.08% and 5.32%.

Table 1. Some characteristics of the used soils. Data reported are the means ± standard deviation.

Soil Classification	Cambisol	Vertisol	Histosol
Textural class	Loamy	Loamy	Sandy loam
pH	7.31 ± 0.04	8.12 ± 0.03	4.71 ± 0.03
Organic Matter	1.08 ± 0.22	1.15 ± 0.27	5.32 ± 0.48
C.E.C (cmol(+)/kg)	10.6 ± 0.7	16.2 ± 0.8	25.6 ± 1.1
Clay %	13.3 ± 0.7	23.0 ± 1.1	10.4 ± 1.0
Silt %	46.4 ± 0.9	42.0 ± 0.7	23.6 ± 0.9
Sand %	40.3 ± 1.2	35.1 ± 1.0	66.0 ± 1.4
Fe %	3.13 ± 0.11	2.44 ± 0.16	4.23 ± 0.15
Total W mg/kg	0.36 ± 0.41	0.29 ± 0.42	0.32 ± 0.42
Total As mg/kg	6.14 ± 1.32	5.83 ± 1.12	4.81 ± 1.12

3.1. Tungstate and Arsenate Sorption

The sorption of tungstate and arsenate in the studied soils, both in single and binary systems, was investigated by determining the sorption isotherms (Figures 1 and 2), in which qe and Ce are expressed in mmol/kg and mmol/L, respectively.

The slopes of the isotherms for both anions vary with solute concentration, highlighting the strong affinity between the anions and the soil surfaces. The isotherms typically exhibit L-type behavior [50], which suggests a decrease in the number of high-affinity sites as sorption progresses. In both the single and binary systems, soils C and V demonstrated lower sorption capacities compared to soil H, a result consistent with the higher pH values in the former two soils.

To describe the isotherms, both the Langmuir and Freundlich models were considered. Although both models adequately represented the experimental data, the Langmuir model exhibited a higher correlation coefficient. Thus, the sorption processes were evaluated using a "Langmuir-type" equation.

$$q_e = \frac{K * qmax * C_e}{1 + K * C_e} \quad (2)$$

where C_e is the concentration of tungstate (arsenate) in solution (mmol/L), q (mmol/kg) is the concentration of tungstate (arsenate) sorbed to the soil, qmax (mmol/kg) is the

maximum adsorption capacity of the soil, and K (L/mmol) is the coefficient related to the bonding energy of tungstate (arsenate) adsorbing sites on soil surfaces.

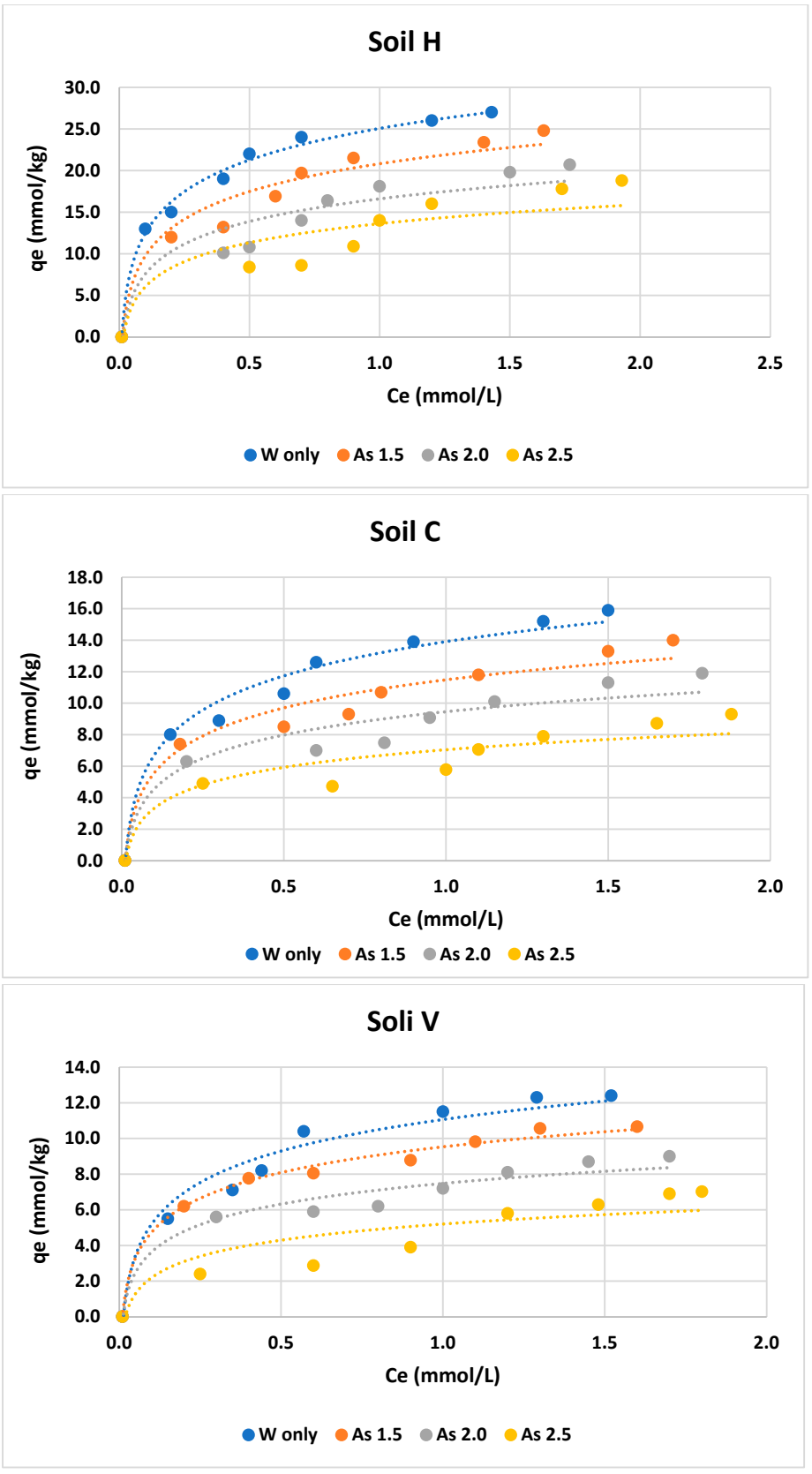


Figure 1. Sorption isotherms of tungstate on the investigated soils in single and binary systems. In the binary systems, 1.5, 2.0, and 2.5 refer to arsenate concentration expressed in mmol/L.

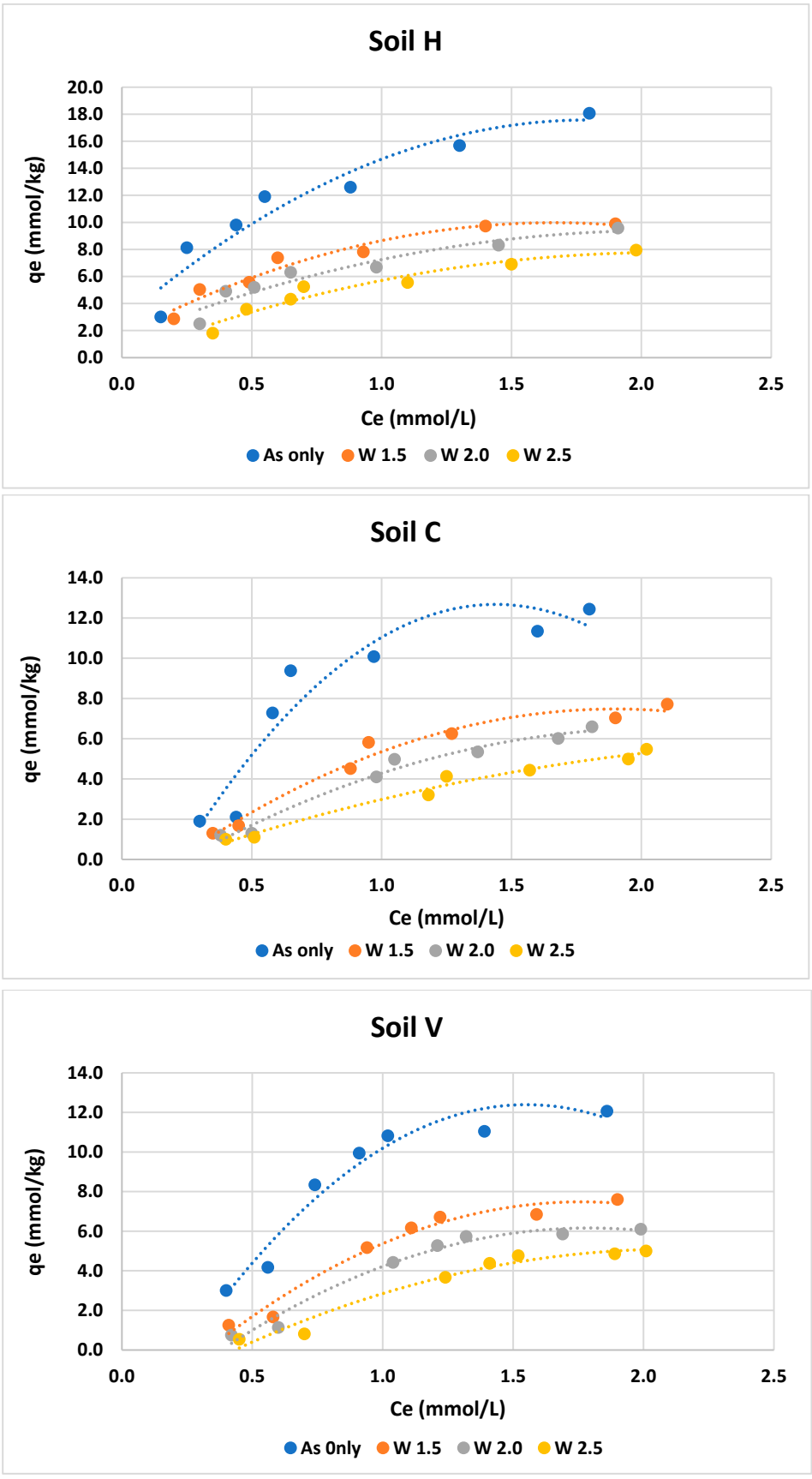


Figure 2. Sorption isotherms of arsenate on the investigated soils in single and binary systems. In the binary systems, 1.5, 2.0, and 2.5 refer to tungstate concentration expressed in mmol/L.

The Langmuir model is based on the assumption that the bonding energy of all sorbing sites is uniform. This is often not the case in soils, where more than one kind of reacting surface occurs. Theoretically, the Langmuir equation was developed to describe the adsorption of a gas on a solid. However, when the sorption isotherm approaches saturation, the conditions enable us to describe the sorption process with a "Langmuir-type" equation, which is one of the most commonly utilized in soil science [51,52].

3.2. Tungstate Sorption

In both the single and binary systems, the shapes of the isotherms were similar, though the maximum sorption varied in the presence of the co-occurring arsenate anion. Tungsten sorption decreased as arsenate concentration increased. The sorption of tungstate on soils is attributed to different bonding strengths, with both inner- and outer-sphere complexes forming simultaneously [51,53,54].

The trend in the isotherms suggests that at low tungstate concentrations, strong specific interactions with soil surfaces occur, leading to the formation of inner-sphere surface complexes. In this scenario, the co-occurring arsenate is unable to compete effectively with tungsten for these specific sorption sites. However, at higher tungstate concentrations, the W sorption mechanism likely shifts toward exchange reactions, resulting in the formation of outer-sphere surface complexes [54,55]. The tungstate bonds with soil surfaces become weaker, facilitating the release of tungstate through exchange reactions with arsenate. Similar patterns of strong inner-sphere and weaker outer-sphere complexes have been observed for anions similar to tungstate and arsenate, such as molybdate [56] and phosphate [57].

Changes in arsenate concentration can influence the sorption process by affecting the competition between tungstate and arsenate for available soil surface sites. As with the interactions between arsenate and phosphate [58–60], the reduction in tungstate sorption with increasing arsenate concentration can be attributed primarily to competition involving outer-sphere complexes. However, stronger inner-sphere complexes may also be involved in this competition. The Langmuir parameters for the single and binary systems are presented in Table 2.

Table 2. The Langmuir parameters of W sorption for single and binary systems, where qmax is the maximum sorption capacity of soils (mmol/kg), K is the constant of the Langmuir equation (L/mmol), and R^2 is the correlation coefficient.

Soil	K	qmax	R^2
H			
W single	0.224	37.1	0.9985
W + 1.5As	0.248	28.8	0.9976
W + 2.0As	0.260	24.3	0.9980
W + 2.5As	0.382	23.8	0.9895
C			
W single	0.246	18.5	0.9960
W + 1.5As	0.270	16.7	0.9930
W + 2.0As	0.303	14.3	0.9949
W + 2.5As	0.354	11.5	0.9953
V			
W single	0.270	15.0	0.9907
W + 1.5As	0.291	13.8	0.9689
W + 2.0As	0.312	11.7	0.9725
W + 2.5As	0.390	9.29	0.9650

In all soils, the qmax value of tungstate decreased in the presence of co-occurring arsenate anions. In soil H, the reduction in qmax was 22.3% with 1.5 mmol of arsenic and 35.8% with 2.5 mmol of arsenic. For soil C, the reduction was 9.7% with 1.5 mmol of arsenic

and 37.8% with 2.5 mmol of arsenic. Similar results were observed for soil V, with reductions of 8% and 38.1% in the presence of 1.5 mmol and 2.5 mmol of arsenic, respectively.

The increased values of the Langmuir constant K can be attributed to the tendency of arsenic to compete with tungsten for non-specific sites. Consequently, most of the remaining tungsten that binds to soil surfaces is more energetically bound, primarily through specific sorption reactions [61].

These results indicate that in acidic soils, the influence of arsenic is substantial, even at the lowest concentration added (1.5 mmol). As the concentration of arsenic increases, the competitive effect becomes more pronounced, especially as soil pH rises. By comparing the maximum tungsten adsorption capacity in the single-component system (qmax(s)) to that in the binary system (qmax(b)), the influence of arsenic–tungsten interaction on the adsorption process can be assessed as follows [61]:

- qmax(b)/qmax(s) > 1: The presence of a competing anion enhances sorption.
- qmax(b)/qmax(s) = 1: The presence of a competing anion shows no discernible interaction effect.
- qmax(b)/qmax(s) < 1: The presence of a competing anion inhibits sorption.

As shown in Table 3, all the ratios for the three binary systems were less than one, indicating that the presence of arsenate reduced tungstate adsorption due to competition between the two anions. Even if the results from the three soils cannot be generalized to different kinds of soil and environmental situations (for example, different land use), the results highlight the importance of soil characteristics on sorption. In particular, when characteristics such as pH or organic matter directly affect the chemistry of tungsten in the soil. In these cases, sorption processes are also favored in other types of soil under acidic conditions or with a high humic substance content, as observed in this experiment.

Table 3. Competition effects of As on the sorption of W as defined by the ratio qmax(b)/qmax(s). For each soil, mean values are reported, and different letters in each row indicate significant differences using one-way ANOVA ($p < 0.05$).

As Added (mmol/L)	qmax(b)/qmax(s)		
	Soil H	**Soil C**	**Soil V**
1.5	0.776 c	0.884 c	0.920 c
2.0	0.655 b	0.757 b	0.780 b
2.5	0.642 a	0.608 a	0.621 a

To evaluate the influence of soil properties on metal sorption capacity, linear regressions were performed between the qmax values experimentally obtained and various soil properties. The data show that sorption capacity, as expressed by qmax values, is mainly influenced by pH, clay content, organic matter content, and iron content across all three soils studied. The results are presented in Table 4. While the high R^2 values are partly due to the limited number of soils investigated, the trends remain consistent. The presence of a competing anion did not alter these trends, only the numerical values.

Soil pH is the utmost critical factor in affecting the properties of soil phases and the W solubility. The data showed that sorption decreased as soil pH values increased, consistent with previous studies on sorption trends in various soil types and soil mineral components, such as iron oxy-hydroxide [28,51,54,62–64]. This decrease in adsorption may result from enhanced competition between OH^- ions and tungstate for the same sorption sites [65] and the increased electrostatic repulsion between tungstate and the solid surfaces [66].

The qmax values were also correlated with the soil organic matter contents. The highest qmax values were observed in soil H, followed by soils C and V. This result aligns with prior research on tungsten sorption in Italian soils [51] and various organic materials, attributed to the stability of complexes formed between W and organic matter [24]. The impact of clay minerals on qmax can be attributed to the reactions of tungstate ions with

hydroxyl groups at the edges of clay structures [24]. The qmax values showed a positive correlation with the clay content of the studied soils.

Table 4. The linear regressions of tungsten qmax against soil characteristics.

Soil Properties	Equation	R^2
pH	single qmax = −6.661 pH + 68.1	0.993
	As 1.5 qmax = −4.471 pH + 49.7	0.994
	As 2.0 qmax = −3.740 pH + 41.8	0.992
	As 2.5 qmax = −4.382 pH + 44.2	0.994
OM	single qmax = 4.808 OM + 11.5	0.944
	As 1.5 qmax = 3.201 OM + 11.8	0.942
	As 2.0 qmax = 2.669 OM + 10.1	0.960
	As 2.5 qmax = 3.167 OM + 6.94	0.961
Clay	single qmax = 1.795 clay − 4.41	0.998
	As 1.5 qmax = 1.205 clay + 1.01	0.997
	As 2.0 qmax = 1.008 clay + 1.08	0.994
	As 2.5 qmax = 1.181 clay − 3.52	0.993
Fe	single qmax = 12.690 Fe − 17.5	0.974
	As 1.5 qmax = 8.571 Fe − 7.94	0.976
	As 2.0 qmax = 7.186 Fe − 6.47	0.961
	As 2.5 qmax = 8.339 Fe − 12.1	0.960

In line with the general behavior of anion sorption on variable-charge soils, iron oxides play a crucial role in the sorption of WO_4^{2-} [20,25,60]. Similarly, in the studied soils, qmax values were well correlated with iron content.

The attraction of tungstate for soil surfaces was also manifested in the distribution coefficient Kd. The distribution coefficient, defined as the ratio of tungstate concentration in the soil solid phase to that in the equilibrium solution, is a suitable parameter for comparing the sorptive properties of the soils under experimental conditions [67]. Kd characterizes the net result of sorption processes and is particularly useful when the presence of another anion creates competition for sorption sites [68]. Additionally, the distribution of tungstate between the solid and solution phases in the soil is crucial for evaluating its mobility and potential bioavailability. A higher Kd value indicates high element retention by the soil surfaces through chemical reactions, leading to low element bioavailability. Conversely, a decrease in Kd values suggests higher potential bioavailability due to the increased presence of the element in the liquid soil phase. For each soil, higher Kd values were observed at lower tungstate concentrations, which can be attributed to the presence of sorption sites with high selectivity, also characterized by relatively strong bonding energies [68].

The Kd of tungstate is significantly affected by the sorption system, whether single or binary. When comparing the Kd values of the soils under competitive sorption of tungstate with those in the single sorption system, the Kd values were lower in the binary systems.

The distribution coefficient medium (Kdm) was calculated across the entire range of added tungstate concentrations [67] in both single and binary systems, highlighting the differences in sorption among the investigated soils. The data are presented in Figure 3.

Our results indicate that the highest Kdm value was observed in the acidic soil (H), while the lowest was found in the most alkaline soil (V). In all soil types, the Kdm values decreased as the concentration of the competing arsenate anion increased from 1.5 to 2.5 mmol.

The sorption of tungsten in binary systems across different soils has been scarcely studied, making it difficult to compare our findings with other experiments conducted under varying soil conditions. However, our results align with previous column studies by Bednar et al. [62], which demonstrated that phosphate competes more effectively with tungstate at acidic pH levels compared to neutral or basic pH. A similar pH-related effect has been reported for ferrihydrite in the competition between tungstate and molybdate.

Conversely, the opposite effect of pH was observed for the sorption of these anions on gibbsite [69]. In general, significant suppressive effects of competing elements on sorption in soils have been frequently documented, both for other anions and for different elements [70,71].

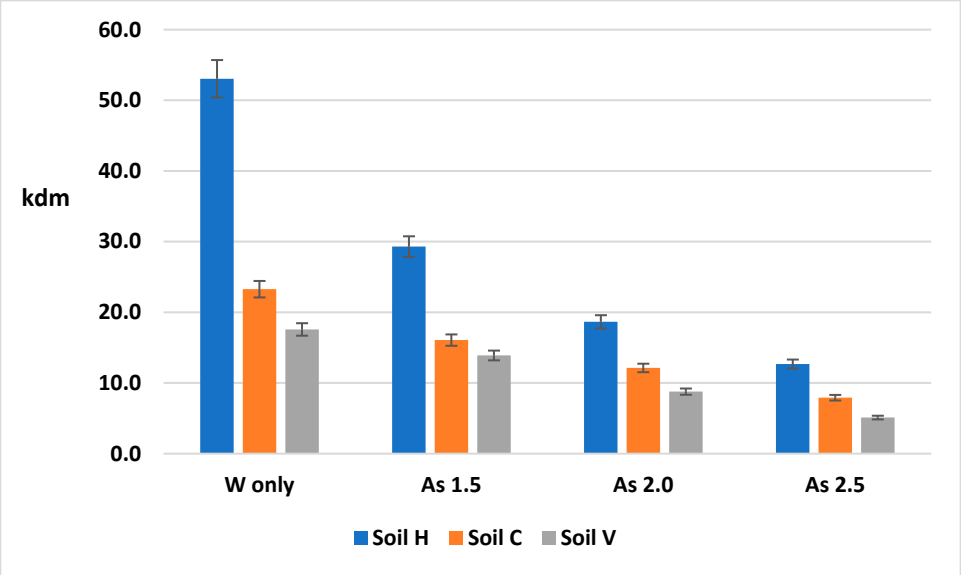


Figure 3. Trend of Kdm (L/kg) in the different soils.

3.3. Arsenate Sorption

As mentioned in the introduction, this article primarily focuses on the competition between tungstate and arsenate for sorption sites in soils rather than providing an in-depth analysis of arsenic sorption itself.

Briefly, the trend of arsenate sorption in the three soils, both in single and binary systems, closely resembles that of tungsten, as shown in Figure 2. The isotherms for arsenate sorption, both individually and in the presence of increasing concentrations of tungstate, can be classified as L-type and are well-described by a Langmuir-type equation. The Langmuir parameters are presented in Table 5.

Table 5. The Langmuir parameters of As sorption for single and binary systems, where qmax is the maximum sorption capacity of soils (mmol/kg), K is the constant of the Langmuir equation (L/mmol), and R^2 is the correlation coefficient.

Soil	K	qmax	R^2
H			
As single	0.183	27.2	0.9337
As + 1.5W	0.188	12.6	0.9833
As + 2.0W	0.191	11.9	0.9695
As + 2.5W	0.198	10.4	0.9713
C			
As single	0.153	15.8	0.9828
As + 1.5W	0.163	10.9	0.9634
As + 2.0W	0.171	8.59	0.9863
As + 2.5W	0.182	7.51	0.9755
V			
As single	0.144	14.6	0.9754
As + 1.5W	0.153	11.7	0.9603
As + 2.0W	0.166	8.22	0.9734
As + 2.5W	0.175	6.36	0.9923

Similar to tungstate, the sorption of arsenate is highest in the acidic soil (H) and decreases in the C and V soils. The maximum sorption values (qmax) for arsenate are consistently lower than those for tungstate and tend to decrease further in the binary system as tungstate concentrations increase.

In the studied soils, the effect of the competing anion on arsenate qmax showed a decrease ranging from 53.7% (W 1.5 mM) to 61.8% (W 2.5 mM) for soil H, 31.0% (W 1.5 mM) to 52.5% (W 2.5 mM) for soil C, and 19.9% (W 1.5 mM) to 56.4% (W 2.5 mM) for soil V.

The effects of soil properties on arsenate sorption, much like those on tungstate sorption, can be analyzed through the relationship with qmax values in both single and binary systems (Table 6).

Table 6. The linear regressions of qmax against soil characteristics.

Soil Properties	Equation	R^2
pH	single qmax = −3.873 pH + 45.1	0.993
	W 1.5 qmax = −0.361 pH + 14.1	0.994
	W 2.0 qmax = −1.129 pH + 17.1	0.992
	W 2.5 qmax = −1.169 pH + 15.9	0.994
OM	single qmax = 2.836 OM + 12.1	0.981
	W 1.5 qmax = 0.308 OM + 10.9	0.986
	W 2.0 qmax = 0.826 OM + 7.51	0.986
	W 2.5 qmax = 0.818 OM + 6.04	0.990
Clay	single qmax = 1.044 clay + 2.94	0.992
	W 1.5 qmax = 0.0976 clay + 10.2	0.988
	W 2.0 qmax = 0.304 clay + 4.83	0.979
	W 2.5 qmax = 0.315 clay + 3.19	0.984
Fe	single qmax = 7.299 Fe − 4.40	0.933
	W 1.5 qmax = 0.593 Fe + 9.81	0.923
	W 2.0 qmax = 2.130 Fe + 2.68	0.891
	W 2.5 qmax = 2.278 Fe + 0.722	0.912

The results obtained, which closely resemble those of tungstate, align with previous studies on arsenic sorption. Specifically, arsenate sorption tends to increase with higher organic matter content in soils [72–74]. Arsenate sorption decreases significantly with increasing soil pH values, in accordance with findings by Rahman et al. [75] and Fan et al. [76]. Higher iron and clay content also enhances arsenate sorption, consistent with prior studies [77,78].

The interaction between arsenate and tungstate during the sorption process was evaluated similarly to tungsten sorption, with the ratio qmax(b)/qmax(s) reported in Table 7.

Table 7. Competition effects of W on the sorption of As as defined by the ratio qmax(b)/qmax(s). For each soil, mean values are reported, and different letters in each row indicate significant differences using one-way ANOVA ($p < 0.05$).

W Added (mmol/L)	qmax(b)/qmax(s)		
	Soil H	Soil C	Soil V
1.5	0.463 c	0.690 c	0.801 c
2.0	0.438 b	0.544 b	0.563 b
2.5	0.382 a	0.475 a	0.436 a

The presence of tungstate as a competing anion reduced arsenate sorption, as indicated by ratio values less than one, highlighting the competition between the two anions for the same sorption sites.

When comparing the qmax values for tungstate, it becomes evident that arsenate is more affected by the competition than tungstate. The percentage decrease in qmax for arsenate in the presence of increasing tungstate concentrations is consistently greater than the decrease in tungstate qmax when arsenate concentrations are increased. These results are detailed in Table 8.

Table 8. Percentage reduction in qmax in the presence of increased concentrations of added competing anion from 1.5 mmol/L to 2.5 mmol/L.

Competing Anion Added	1.5 mmol/L		2.0 mmol/L		2.5 mmol/L	
	As	W	As	W	As	W
Soil H	53.7	22.4	56.3	34.5	61.8	35.8
Soil C	31.0	9.73	45.6	22.7	52.5	37.8
Soil V	19.9	8.00	43.7	22.0	56.4	38.1

These differences between single and binary systems can be attributed to the ability of both anions to form inner- and outer-sphere complexes with the soils under investigation [79]. The observed decreases in sorption can be ascribed to competition for sorption sites, both non-specific and specific, which exhibit a high affinity for both anions. At lower concentrations of the competing anion (1.5 mM), the competition effect is reduced due to the high availability of sorption sites for both anions. However, as the concentration of the competing anion increases (2.0 and 2.5 mM), competition for available sorption sites intensifies, leading to a reduction in the sorption of each anion compared to the single-system scenario.

Interestingly, arsenate had little effect on W sorption in soils C and V, where W is likely to be involved in specific sorption due to the lower sorptive characteristics of these soils (e.g., increasing pH, etc.).

The distribution coefficient (Kd) serves as a useful index for comparing the sorptive capacities of soils under similar experimental conditions. The trend of the medium Kd (Kdm) in each soil for arsenate sorption is illustrated in Figure 4.

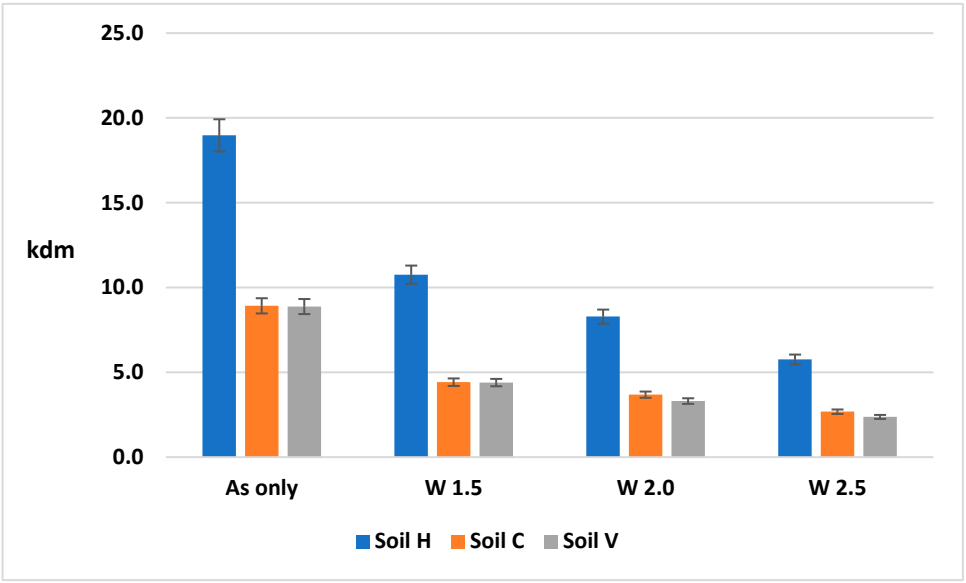


Figure 4. Trend of Kdm (L/kg) in the three studied soils.

In the single systems, for all three soils, the Kdm values of arsenate are lower than those of tungstate, indicating that a significant amount of arsenate remains in the soil solution. As the concentration of added tungstate increases, the Kdm values further

decrease, highlighting the competitive interaction between the two anions, similar to the behavior observed for tungstate in previous experiments.

4. Conclusions

Sustainable development heavily relies on critical elements, including tungsten. As a result, tungsten's presence in the environment is expected to increase. Soil plays a vital role in protecting groundwater quality and ensuring safe food production. Therefore, understanding the fate of tungsten in soil is key to comprehending its bioavailability pathways, which are directly linked to human health. The main processes that determine bioavailability are sorption mechanisms, which dictate the distribution of elements between the solid and liquid phases of soil. Research on tungsten in European soils is still limited. Our study addresses the competitive sorption between tungsten and arsenic, two elements whose simultaneous presence in soils of varying origins and characteristics is likely to rise due to the increasing use of tungsten in sustainable industrial activities.

Both tungstate and arsenate sorption isotherms display L-type behavior, indicating a reduction in the number of high-affinity sites as sorption progresses. This suggests a strong affinity between the anions and soil surfaces, with the highest sorption occurring in the acidic soil (H) and the lowest in the most alkaline soil (V). This behavior is effective for both elements studied. In the case of W, the maximum sorption in the more acidic soil is more than double the value in the more basic soil, both in the absence and presence of arsenic. In the case of As, the maximum sorption in acidic soil is over 1.5 times that in more basic soil, both in single and binary systems. Although the presence of arsenate significantly reduces tungstate sorption, arsenate is more affected by the competition than tungstate.

While our study on three soils cannot be extended to other soil types, data emphasize that soil properties are crucial in determining tungsten sorption. Further studies on the simultaneous sorption of these two anions are needed to inform environmental legislation, which currently pays little attention to the presence of tungsten in soil. It would be important to increase the knowledge of tungsten concentrations in soils, which is currently very limited, as well as to evaluate the mobile and bioavailable forms.

Although this study primarily focuses on tungsten, it is important to note that the competition between these two anions can lead to an increase in the concentration of arsenic in the liquid phase of the soil. This, in turn, may raise the bioavailable concentration of this highly dangerous element.

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