

Article

Adsorption, Desorption and Bioavailability of Tungstate in Mediterranean Soils

Gianniantonio Petruzzelli * and Francesca Pedron

Institute of Research on Terrestrial Ecosystems (IRET), National Council of Research, 56124 Pisa, Italy; francesca.pedron@cnr.it

* Correspondence: gianniantonio.petruzzelli@cnr.it

Received: 30 July 2020; Accepted: 19 August 2020; Published: 22 August 2020



Abstract: The adsorption and desorption process of the tungstate ion was studied in three soils characteristic of the Mediterranean area, with particular reference to bioavailability pathways. In the three soils examined, the tungstate adsorption was described by a Langmuir-type equation, while the desorption process showed that not all the adsorbed tungstate was released, probably due to the formation of different bonds with the adsorbing soil surfaces. The pH was found to be the main soil property that regulates the adsorption/desorption: The maximum adsorption occurred in the soil with the acidic pH, and the maximum desorption in the most basic soil. In addition, the organic matter content played a fundamental role in the adsorption of tungstate by soils, being positively correlated with the maximum of adsorption. These results indicate that the lowest bioavailability should be expected in the acidic soil characterized by the highest adsorption capacity. This is confirmed by the trend of the maximum buffer capacity (MBC) of soils which is inversely related to bioavailability, and was the highest in the acidic soil and the lowest in the most basic soil. Our data could contribute in drafting environmental regulations for tungsten that are currently lacking for Mediterranean soils.

Keywords: tungsten adsorption; tungsten desorption; batch adsorption; Langmuir equation; soil characteristics

1. Introduction

Tungsten (W) is a transition metal in the VI group of the periodic table of elements, together with chromium and molybdenum. Since its discovery in the late 1700s, tungsten has been used in many industrial productions, including domestic goods and highly specialized components of “high tech” equipment [1]. What make this element particularly attractive for industrial production are its melting point (the highest of all metals), its resistance to corrosion agents, and its property as a good electrical conductor. Tungsten is also widely used as a catalyst in many chemical reactions, and as a result, more than 33,000 t of tungsten are annually consumed by industry [2].

Tungsten is naturally present in the environment mainly in minerals such as Wolframite (Mn and Fe tungstate $\text{FeWO}_4/\text{MnWO}_4$) and Scheelite (CaWO_4). Generally, its oxidation states 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 [1,3,4]. Tungsten chemistry is one of the most complex in soil due to the many possibilities of ways it forms soluble complexes with inorganic and organic ligands [5,6]. Tungsten anions can polymerize in various environmental compartments and under certain physiological conditions also in living organisms. These reactions lead to the development of polyoxyanions, which can have different chemical properties from monotungstates [7].

The toxicological profile of tungsten is still incomplete. However, the element is no longer considered inert as in the past and now adverse effects on humans and the environment have been recognized [1,8,9]. In fact, tungsten studies increased due to the discovery of cases of leukemia

in Fallon in Nevada that were attributed to the presence of tungsten in the environment [10,11]. The aspects related to human health are of growing concern, due to the increasing military utilization of the element both, as an alternative to lead-based munitions [12] and as a replacement for depleted uranium in many military applications [13]. In 2016, tungsten was identified as presenting potential danger to public health and was reported in the EPA National Priorities List [14] with particular attention to the speciation of the element, since polytungstates are considered much more toxic than monotungstates [3,7].

The earth's crust is by far the most significant source of tungsten. In soil the concentration of tungsten ranges from 0.5 to 83 mg·kg⁻¹ with a reduced concentration in surface layers from 0.2 to 5 mg·kg⁻¹ [15]. Tungsten compounds have also been found in groundwater in the vicinity of both natural and anthropogenic sources. Under certain conditions (for example a high soil pH), tungsten can dissolve in water and leach along the soil profile into groundwater. It can also potentially bioaccumulate in the trophic chain [16].

Pollution from mines and industrial excavation may contribute to the presence of tungsten in soil [2], as well as military operations, and waste production from the electronics industry [17]. The fate and transport of tungstate in soil depends above all on the processes of adsorption/desorption on the solid phase. Adsorption studies have mostly investigated the process on soil components such as silicate clay minerals [18–20] or metal oxides [21–25] to evaluate the interactions and the linkages between tungsten compounds and soil surfaces.

Understanding the adsorption processes of tungsten compounds in soils helps in evaluating the bioavailability and, therefore, the potential toxicity of tungsten for organisms, including humans. Plants, for example, can absorb tungstate in fairly high quantities according to the genotype of the plant and soil characteristics [3]. Despite the growing number of studies on tungsten in the environment, information on the characteristics of adsorption-desorption of tungsten on soils of the Mediterranean area is relatively scarce. In a previous work, we evaluated the adsorption processes of tungstate in Italian soils [26]. In this work, we have extended the survey to soils of the Mediterranean area, also introducing desorption processes. Desorption is in fact a process of great importance for the evaluation of the bioavailability of chemical substances, and also provides important indications for the drafting of environmental regulations related to the soil and the food chain.

The aim of this study was to provide data on the adsorption and desorption of tungstate in three Mediterranean soils, characterized by different properties focusing on bioavailability, and the potential transfer of the element from soil to the food chain.

2. Materials and Methods

2.1. Soils

The Mediterranean climate is characterized by rainy winters with warm and dry summer months with water shortages and the drying out of vegetation and soils. Many kinds of soil exist in the Mediterranean area, characterized by different properties. For this study soil samples were collected at a depth of about 0 to 20 cm. The soil TH was collected in southern France and can be classified, according to the USDA Soil Taxonomy, as Typic Hapludalf, soil TE was collected in central Italy (Typic Eutrochrept), and soil EH was collected southern Spain (Entic Hapludoll).

The soil samples were air-dried and ground to pass through a 2-mm sieve to determine various selected properties. Soil pH (soil/water ratio of 1:2.5), organic matter (OM) and cation exchange capacity (CEC) were determined according to the Chemical Methods of Soil Analysis of Soil Science Society of America [27], whereas the specific surface area (SSA) and particle-size distribution were determined according to the Physical Methods of Soil Analysis of Soil Science Society of America [28].

2.2. Adsorption Desorption Experiments

For the adsorption study, 1 g of soil sample and 25 mL of solution containing increasing concentrations of sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$) from 0.2 to 2.5 $\text{mmol} \cdot \text{L}^{-1}$ were transferred into 60 mL polypropylene centrifuge tubes. To evaluate the best equilibration time, adsorption and desorption experiments were carried out with different contact times using the highest initial tungstate ions WO_4^{2-} concentration 2.5 $\text{mmol} \cdot \text{L}^{-1}$. Samples were collected at 0, 0.5, 1, 2, 4, 6, 9, 12, 15, 18, 21 and 24 h for the tungsten analysis. On the basis of the results solutions were stirred at 288 K for 18 h to reach the adsorption equilibrium, and for 24 h for desorption step. Suspensions were centrifuged at 9500 rpm for 15 min, then the clear liquid supernatant was filtered through 0.2 mm Whatman filter paper for the analyses. The experiments were carried out in triplicate.

The amount of tungstate (WO_4^{2-}) adsorbed per mass of soil was calculated by the difference between the quantity added and that recovered in the equilibrium solution, according to the equation,

$$q = [V \times (C_i - C_e)]/m, \quad (1)$$

where q = the amount of tungstate adsorbed per unit mass of soil ($\text{mmol} \cdot \text{kg}^{-1}$), C_i = the initial tungstate concentration ($\text{mmol} \cdot \text{L}^{-1}$), C_e = the WO_4^{2-} concentration at equilibrium ($\text{mmol} \cdot \text{L}^{-1}$), V = the volume of WO_4^{2-} solution added (mL), and m = the mass of soil used (g).

Desorption was carried out for each soil sample remaining after the centrifugation by adding a 0.01 M CaCl_2 solution to the residual soil. After the adsorption step, the supernatant was removed and 25 mL of 0.01 M CaCl_2 solution was added to dry soil. The soil-water suspension was shaken for 24 h at 288 K and centrifuged at 9500 rpm for 15 min, then the supernatant was filtered through 0.2 mm Whatman filter paper for the analyses. This extractant, 0.01 M CaCl_2 , is considered representative of the concentration of tungstate in soil solution [7]. The mixture was re-suspended and stirred at the same temperature 288 K for 24 h. The suspension was centrifuged and the supernatant solution was collected for W tungsten analysis, to determine the concentration of WO_4^{2-} desorbed.

To evaluate the effect of ionic strength on the adsorption, supplementary adsorption trials were performed with the same procedure previously described, but with the addition of ammonium chloride (NH_4Cl) at concentrations of 0.05 M and 0.1 M to the WO_4^{2-} solutions equilibrated with the soils. In all the experiments no adjustment of pH was carried out whichever the solution added, such as 0.01 M CaCl_2 and ammonium chloride (NH_4Cl) original soil pH values remained unchanged after equilibration in all cases.

2.3. Tungsten Analysis

Concentrations of tungstate in the supernatants of the adsorption and desorption experiments were measured by inductively coupled plasma optical emission spectroscopy (ICPOES Varian AX Liberty Varian Milano, Italy). Operating parameters wavelength 239.709 nm. Plasma flow = 16.5 $\text{L} \cdot \text{min}^{-1}$ Auxiliary flow = 2.25 $\text{L} \cdot \text{min}^{-1}$. The original tungsten concentration in the soils was determined by the USEPA method 3050B following, the modified digestion procedure with the addition of phosphoric acid to nitric acid developed by Dermatas [29] and described by Bednar [30]. This step is necessary because the specific tungsten properties can promote the formation of insoluble species under acidic conditions [7]. This method is a variation of the OSHA method ID-213. All chemicals used were of reagent grade.

Quality assurance and quality control were performed by: Verification of the linearity of the calibration line, verification of the reagent blank immediately after the calibration line, testing a standard solution every 10 samples and at the end of the analytical sequence. A certified reference soil material (NIST SRM 2710) was used to control the quality of the analytical procedure. The limit of detection (LOD) and the limit of quantification (LOQ) for WO_4^{2-} were 0.02 $\text{mg} \cdot \text{L}^{-1}$ and 0.05 $\text{mg} \cdot \text{L}^{-1}$ respectively. The recovery of spiked samples ranged from 95% to 101% with an RSD of 1.89 of the mean.

Statistical analysis was performed using STATISTICA version 6.0 (Statsoft, Inc., Tulsa, OK, USA).

3. Results

The main properties of the soils are reported in Table 1. The soils show different properties, but with a similar tungsten content below $0.5 \text{ mg}\cdot\text{kg}^{-1}$.

Table 1. Various properties of the soils used.

Parameters	Soil TE	Soil EH	Soil TH
Soil classification	Typic Eutrochrept	Entic Hapludoll	Typic Hapludalf
pH	4.7	7.1	8.0
Organic Matter	5.32	2.10	1.43
C.E.C (cmol (+) kg^{-1})	25.6	17.7	16.6
Clay%	10.4	12.5	7.65
Silt%	23.6	28.8	14.0
Sand%	66.0	59.3	78.3
Total W $\text{mg}\cdot\text{kg}^{-1}$	0.32	0.44	0.29
SSA ($\text{m}^2\cdot\text{g}^{-1}$)	186	169	140
Fe	2.42	2.20	2.15
Al	1.84	2.11	1.98

The soils selected for this experiment were characterized by different pH values ranging from 4.70 to 8.01, and with an organic matter content from 1.43% to 5.32%. The soils were selected on the basis of their characteristics exclusively to evaluate the influence of these on tungsten adsorption. No attempt was made however to deepen their pedological or geological properties despite their strong influence on the soil characteristic. The original tungsten content was very low in all the soils.

3.1. Influence of Contact Time

Tungstate adsorption process can be distinguished into two stages a fast increase in the first 2 or 3 h due to a rapid retention of tungstate followed by a slow adsorption stage after this period of time in which the amount of adsorption increased very slowly. The process seemed to be completed within 12 h, since no variation was detectable for longer contact times in any of the three soils. This behavior, which is often found in soil adsorption studies can be explained by the nearly immediate adsorption on accessible sites followed by a decrease with time of the available adsorption sites on soil surfaces [20,31]. With the same procedure the release of WO_4^{2-} in the desorption step was evaluated, and the process appeared completed in 12 h. The contact time is an operational parameter, however it may significantly influence the estimation of sorption. Consequently, to be sure that the equilibrium had been reached all the experiments were extended by shaking the suspensions for 18 h.

3.2. Modelling Sorption and Desorption of Tungstate by Soil

The adsorption of tungstate in the soils examined was investigated at the original pH of each soil by determining the adsorption isotherms, in which the amount adsorbed (q) is reported versus equilibrium concentration (C_e). In the range of concentrations used in this study, WO_4^{2-} adsorption showed a curvilinear rather than linear behaviour (Figure 1). The value of R^2 for linear isotherm was about 0.70 for all the soils. The non-linear trend is common in soil sorption processes [32,33] and may be related to the existence of different sorption mechanisms in relation to the concentrations of adsorbing species.

The adsorption isotherms of the three soils were analogous (Figure 1) and according to their shapes can be defined of "L type" [34]. Since the polytungstates formation can be expected only at more acidic pH, where up to 50% of the total tungsten may be in polymeric forms [35,36] in the pH range of the used soils, the fully dissociated tungstate ion can be considered the predominant form [37]. The amount of tungstate adsorbed appeared to reach a plateau, indicating that, in the used

experimental conditions, tungstate ions occupied all the available surfaces sites in the soils investigated. The adsorption capacity of the soils greatly diminished, in the order TE > EH > TH.

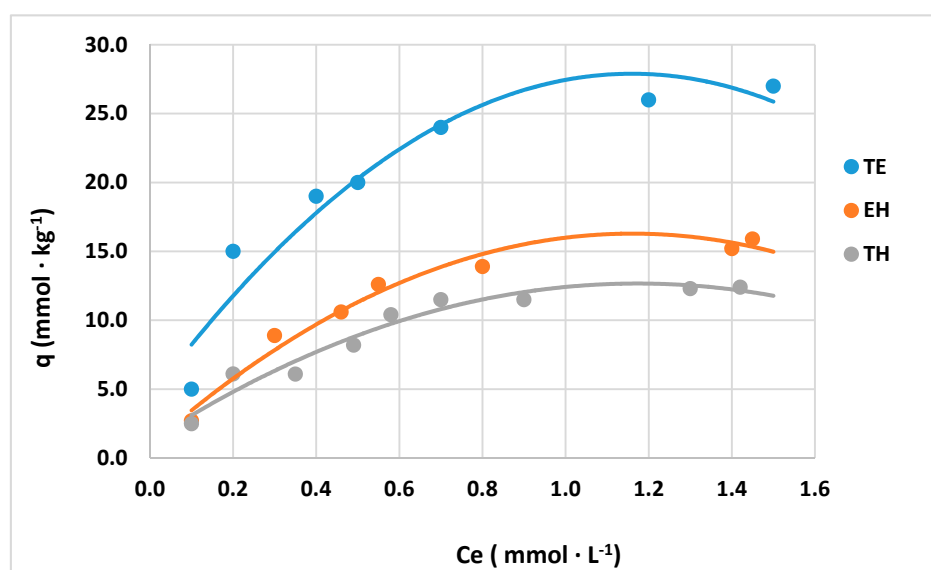


Figure 1. Tungstate adsorption isotherms in the investigated soils.

Several isotherm equations are commonly used to describe sorption processes in soils. Of these, the Langmuir and the Freundlich equations are the most frequently used, to describe the nonlinear sorption processes in soil, due to their wide applicability.

The nonlinear forms of the Langmuir equation is,

$$q = (K \times q_{\max} \times C_e) / (1 + K \times C_e), \quad (2)$$

where C_e is the concentration of tungstate in solution ($\text{mmol}\cdot\text{L}^{-1}$) and q ($\text{mmol}\cdot\text{kg}^{-1}$) is the concentration of tungstate adsorbed to soil, q_{\max} ($\text{mmol}\cdot\text{kg}^{-1}$) is the maximum adsorption capacity of the soil, and K ($\text{L}\cdot\text{mmol}^{-1}$) is the coefficient related to the bonding energy of tungstate adsorbing sites on soil surfaces.

The Freundlich equation is,

$$q = K_f \times C_e^{1/n}, \quad (3)$$

where q and C_e are defined as above, K_f the affinity constant ($\text{mmol}\cdot\text{kg}^{-1})(\text{mmol}\cdot\text{L}^{-1})^{-1/n}$ and $1/n$ the sorption intensity are the Freundlich constants derived from the experimental data which are linked to the adsorptive capacity of soil.

Data from the Langmuir and Freundlich equations are reported in Table 2.

Table 2. Langmuir and Freundlich parameters for the investigated soils.

Soil	Langmuir			Freundlich		
	q_{\max}	K	R^2	$\text{Log } K_f$	$1/n$	R^2
TE	35.08	0.259	0.957	1.421	0.553	0.822
EH	20.66	0.247	0.940	1.193	0.576	0.806
TH	16.15	0.265	0.966	1.0921	0.559	0.865

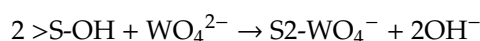
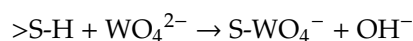
Both equations described the sorption process well. However, the correlation coefficients R^2 of the Langmuir model were higher than those of the Freundlich for all the soils thus the Langmuir equation was selected to describe the WO_4^{2-} sorption. However, it should be noted that in the three soils the

trend of q_{\max} is similar to that of the constant K_f , which represents the adsorbing capacity of the soil in the Freundlich model: The higher q_{\max} , the higher K_f .

Theoretically, the Langmuir approach is based on the statement that the bonding energy of all adsorbing sites is uniform. In soil various kinds of reacting surfaces are involved in the adsorption processes, but the Langmuir equation is one of the most used in soil chemistry when the adsorption approaches saturation. Under our experimental conditions the L-type isotherms obtained can be described by a Langmuir type equation in the range of applied concentrations. The Langmuir equation has been used for the description of tungsten compounds adsorption on different kinds of kaolinite [19,20] and on soils [38].

The WO_4^{2-} behavior, at low concentrations added, could be ascribed to the prevalence of specific adsorption with the formation of inner-sphere surface complexes whereas the higher concentrations of the main mechanism was likely exchange reactions with the formation of outer sphere surface complexes [39]. Strong inner-sphere complexes have also been reported for anion similar to tungstate such as molybdate [40] and phosphate [41]. The same conclusions were also drawn from a study on the adsorption of tungsten and molybdenum on aluminum oxides [21]. The findings indicated that tungstate strongly interacts with the Al_2O_3 surface suggesting a nearly irreversible sorption at lower tungstate addition, on the other hand at higher tungstate loading some of the tungstate is bonded more loosely and can be released by exchange reactions [21].

Anion adsorption on variable charge soil surfaces should be considered as an essential process in tungstate adsorption [3] and can be described according to general anion reactions [19,29,42],



where WO_4^{2-} is the tungstate anion and $>\text{S-OH}$ is a reactive metal hydroxyl group. The same processes are also likely to have occurred in the three investigated soils.

Examination of the isotherms (Figure 1) shows how irrespective of the equilibrium concentration the adsorption of WO_4^{2-} was maximum for the acidic soil (TE) and minimum for the most alkaline soil (TH). These results are in accordance with previous findings concerning tungsten adsorption on different oxides [18,21–23], on clays and peat [19], and soils [38], which showed a high dependence of tungsten adsorption on soil pH. This soil property is the most important in determining both the solubility of tungstate ions and the characteristics of the adsorbing soil surfaces, as reported in the study on three Italian soils, which showed that varying pH of each soil largely determined the amount of WO_4^{2-} adsorbed for the same soil [26].

The maximum adsorption capacity calculated from the Langmuir equation was $10.1 \text{ mmol}\cdot\text{kg}^{-1}$ in Oxisols [20], ranged from 9.06 to $30.7 \text{ mmol}\cdot\text{kg}^{-1}$ in Italian soils [26] and resulted $6.14 \text{ mmol}\cdot\text{kg}^{-1}$ on kaolinite 27.4 , and $22.9 \text{ mg}\cdot\text{kg}^{-1}$ for peat, montmorillonite, respectively [19]. Tungstate adsorption maximum was very higher $226 \text{ mmol}\cdot\text{kg}^{-1}$ onto pure goethite [20]. Thus, our results are similar to those of other soils and much lower than that for pure goethite.

The maximum adsorption was also linked to the organic matter content of the studied soils which was the highest in TE soil with decreasing quantities in EH and TH soils. This result is in agreement with previous studies concerning tungsten adsorption on Italian soils [26] and various organic materials, and is due to the stability of complexes between tungstate and humic substances [19]. As described for similar elements, such as arsenic and antimony [43,44] humic materials with a high binding capacity can greatly influence the adsorption of tungsten on variable charge minerals in soils. Also, the good correlation between the adsorption maximum and the soils CEC is mainly due to the contribution of the organic matter to the CEC.

Iron and aluminum oxy-hydroxides are very important especially in dynamic redox conditions [45] when there are variations in the interactions between organic matter and the oxides and hydroxides of iron on which tungsten can be adsorbed. However, since the content of iron and aluminum

oxy-hydroxides was not very different between the three soils, we were unable to distinguish the influence of these soil components.

The TE soil was also characterized by the highest SSA value, which was the lowest in TH soil and as expected, the adsorption maxima, was related to the soils surface area which decreased in the order $TE > EH > TH$.

Although, the soil texture should be considered as essential in tungstate sorption [3], in the investigated soils, the influence of pH seemed to prevail considerably over other properties, such as the clay content. The lower influence of clay minerals with decreasing pH for tungstate can be ascribed to their net negative surface charges that drastically reduce the sorption ability. This has also been reported in the adsorption process of tungsten compounds from polluted waters, in fact biopolymer are often used to coated clay particles to increase the adsorption of tungsten [46].

3.3. 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 amount that is released by the adsorbing surfaces of the soil in the desorption processes. This bioavailable quantity is therefore determined by the actual concentration in the soil solution and the quantity adsorbed on the soil surfaces. The relationship between these two variables was defined in a seminal article by Holford and Mattingly [47] as the “soil buffer capacity” and determines, in this specific case, the amount of variation in the adsorbed quantity per unit of variation of the concentration of tungsten in the soil solution [47]. The buffer capacity represents a measure of the resistance of the soil to the variation in tungsten concentration in the liquid phase of the soil when adding or subtracting tungsten to/from the soil system, or in other words, the soil’s capacity to moderate changes in tungsten soil solution concentration when tungsten is added to, or removed from, the soil [48].

When tungstate ions are removed from the soil solution, for example by leaching or following uptake by plants, part of the adsorbed tungsten will be transferred to the soil solution to establish a new equilibrium. The release of tungsten from the solid surfaces of the soil is determined by the strength and type of bonds that have formed between the element and the soil surfaces in the adsorption processes, as well as the total quantity adsorbed. The strength of the bonds is represented in the Langmuir equation by the constant K , therefore the buffer capacity will depend both, on the adsorbed quantity (q_{\max}) and on the strength of the bonds with which it is retained in the solid phase of the soil, identifiable by the value of K .

For each soil the maximum buffer capacity (MBC) is defined as the product of q_{\max} and K the Langmuir equation [49]:

$$MBC = q_{\max} \times K. \quad (4)$$

Tungsten plant uptake will be inversely related to MBC, because, being MBC linked to the bonding energy K . the higher the buffer capacity the more difficult will be the release of tungsten in the soil solution from where it can be taken up by plants. The soil buffer capacity, which greatly influences the bioavailability can be obtained from the adsorption isotherms. In fact, when tungsten in soluble form is added to the soil, the metal will tend to adsorb on the surfaces of the soil, and the adsorbed quantity will depend on both the affinity of tungsten for these surfaces and the availability of adsorbing sites. According to equation (4), the MBC [49] for the three investigated soils were 90.5, 51.1 and 42.8 $L \cdot mmol^{-1}$ for TE, EH, and TH, respectively. MBC values suggest that the bioavailability of tungstate in the studied soils will follow the order $TH > EH > TE$.

With respect to bioavailability, desorption processes are just as important as those of adsorption. Thus desorption experiments were carried out to estimate the capability of soil to retain WO_4^{2-} ions after adsorption. The desorption process in soils is crucial to the assessment of the extent of the metal that can be leached, or retained by soil surfaces. Soil desorption was carried out using $CaCl_2$ 0.01 M. This extractant is considered the best to simulate the release of metals in the soil liquid phase since

it well reflects the concentration of soil solution [7]. It must be considered that, in the short-term experiments of adsorption/desorption, the quantity released may underestimate the soil retention capacity, which over time will tend to increase because aging favours the irreversibility of many reactions [50]. For this reason, in this experiment we chose not to use stronger extractants, such as ammonium sulphate [3,51], in order not to overestimate the bioavailability of tungsten.

The trend of WO_4^{2-} desorption from the three soils was examined by plotting the desorbed amount in relation to the amount adsorbed. The desorption trend was similar for the three soils, the amount of WO_4^{2-} released from the soil increases, as the quantity adsorbed in all the soils increase, however the amount of WO_4^{2-} desorbed greatly changed (Figure 2).

The relationship between the amount of tungstate desorbed at each adsorbed concentration for the three soils, can be described by an exponential equation with high values of R^2 (Soil TE = 0.922, EH = 0.985, TH = 0.981). The figures show that the higher the amount adsorbed the higher the tungstate concentration was in the desorbed solution. When the concentration of tungstate was added to the soils was low, the adsorbed quantity was small, but it appeared to be irreversibly retained. In fact, in the desorption solution there were no appreciable concentrations of tungsten for the lowest concentration added.

As in the case of the adsorption, soils pH influenced also the release of WO_4^{2-} from the soil surfaces. Desorption experiments showed that the amount of desorbed W increased with increasing pH of the three soils. Considering the surface charge, with increasing soil pH the positive surface charge decreases and, the linkages of WO_4^{2-} with soil are thus less stable.

At acidic pH (soil TE), the low rate of desorption highlights the increase in the retention of tungstate in the soil solid phase and thus tungstate's reduced mobility. The amount of tungstate that was adsorbed but not desorbed was likely related to strong linkages with soil surfaces, and can be reasonably considered to be not available to plants. In relation to the adsorbed quantity, going from the lowest to the highest concentration adsorbed, the desorbed amount varies from 1% to 11% in soil TE, from 2% to 39% in soil EH, and from 2% to 44% in soil TH (Figure 3).

The results confirm the hypothesis that when added at low concentration, the adsorption of tungstate on the three soils mainly involved strong specific adsorption and the percentage of releasable metal was very low. At increasing concentration of adsorbed tungstate, the higher desorption rate showed the occurrence of non-specific adsorption with lower energy linkages between tungstate and the soil surfaces.

To compare the sorption and desorption trend of the soils, it is possible to consider the parameters TW_{ads} and TW_{des} . These refer to the total amount $\text{mM}\cdot\text{kg}^{-1}$ of WO_4^{2-} adsorbed by, and desorbed from each soil at each WO_4^{2-} equilibrium concentration in the adsorption step [52],

$$TW_{\text{ads}} = \sum_{2.5}^{0.2} C_{\text{ads}}, \quad (5)$$

$$TW_{\text{des}} = \sum_{2.5}^{0.2} C_{\text{des}}, \quad (6)$$

The maximum values of TW_{ads} , as well as the minimum values of TW_{des} , were recorded for soil TE 104 and $5.5 \text{ mM}\cdot\text{kg}^{-1}$ respectively which, had the acidic pH and relatively higher organic matter content (Table 1). On the other hand, the minimum values of TW_{ads} $48.51 \text{ mM}\cdot\text{kg}^{-1}$ was observed in soil TH, with the maximum values of TW_{des} $11.23 \text{ mM}\cdot\text{kg}^{-1}$. This soil showed the highest pH and the lowest organic matter content. Intermediate values were observed for EH soil with the values of 61.19 and $10.68 \text{ mM}\cdot\text{kg}^{-1}$ for TW_{ads} and TW_{des} respectively. The trend of TW_{ads} and TW_{des} provide an interesting contribute to understand the bioavailability of tungsten since they correlated well both positively and negatively with the buffer capacity of soils expressed as MBC. In Figure 4 the trend of MBC versus TW_{ads} and TW_{des} is reported.

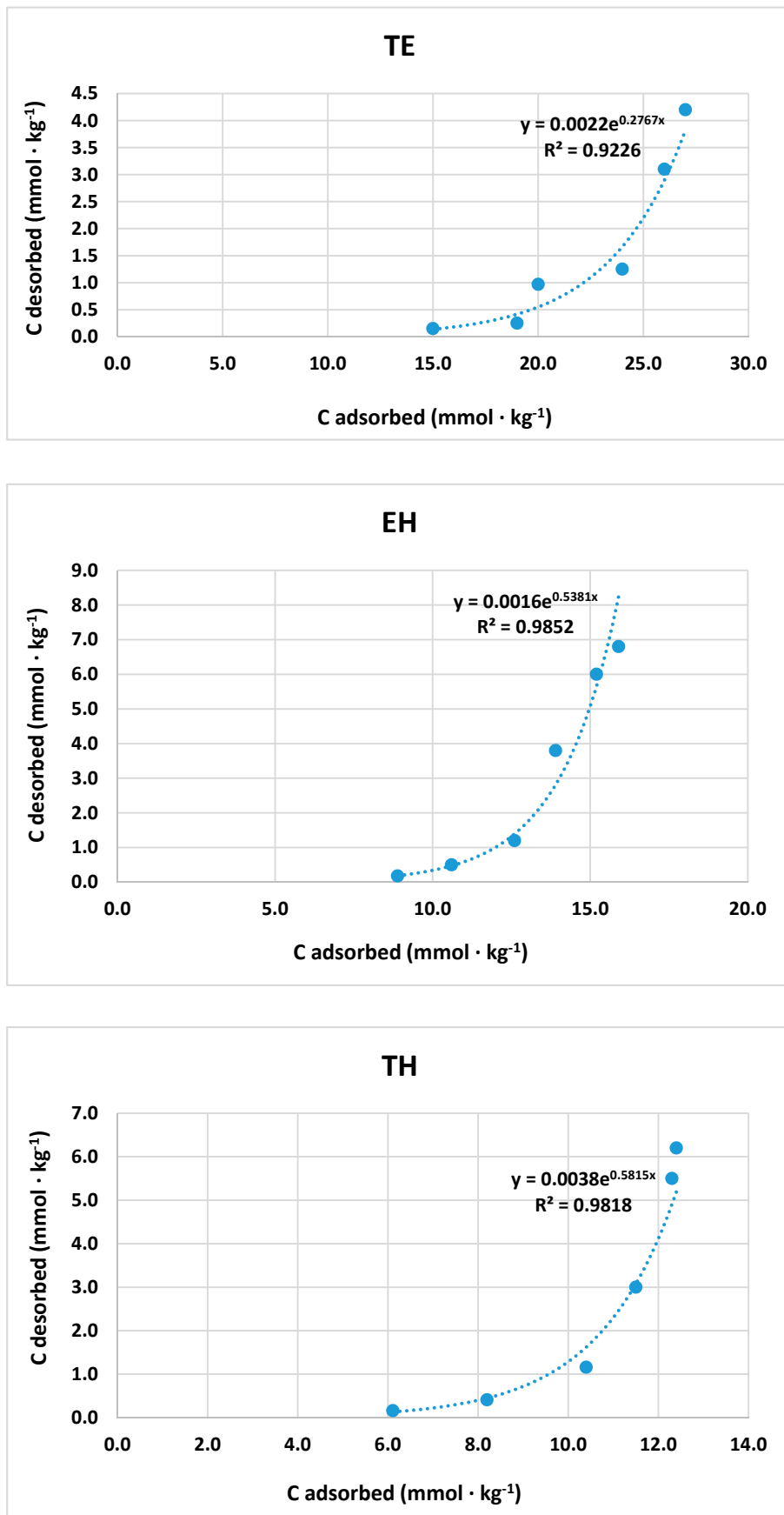


Figure 2. The relationship between tungstate adsorption and desorption in the three soils TE, EH and TH.

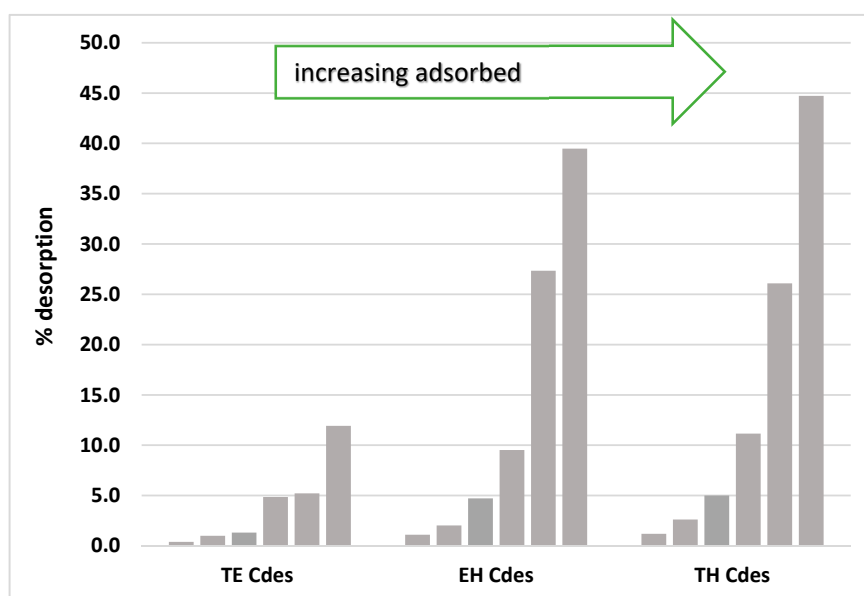


Figure 3. Desorption percentage in the three soils in relation to increasing adsorbed quantities.

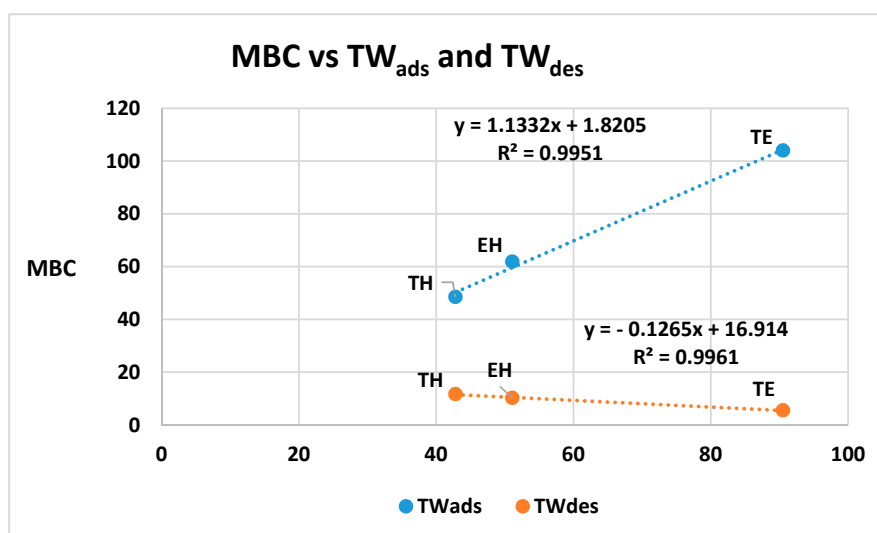


Figure 4. Trend of Maximum Buffer Capacity (MBC) vs. total tungstate adsorbed (TW_{ads}) and desorbed (TW_{des}) amounts.

These results further confirm the existence of both, a specific and non-specific adsorption mechanisms of tungstate in soils, with some nearly irreversible binding of tungsten by soil surfaces at low addition of this element, until the buffer capacity of soils can counteract the variations in the equilibrium concentration between the liquid and solid phases of soils.

This adsorption/desorption hysteresis of tungstate has been reported also for many metals, metalloids, and organic compounds in soil [53–55] and can be related to the concurrent reactions of tungstate with different kinds of adsorbing sites in soil [56].

The existence of different linkages following the adsorption of tungstate on the investigated soils was confirmed by the experiments carried out at different ionic strength. The effect of the background electrolyte at different concentrations is commonly utilized to distinguish the inner-sphere from the outer-sphere complexes. The adsorption process is influenced by the variation of the background electrolyte concentration due to changes in the activity of adsorbing anions and the competition of the

electrolyte ions and adsorbing anions for the same surface sites of the soil. Thus, strongly bonded inner-sphere complexes are hardly influenced by changing ionic strength, while weakly bonded anions to soil surfaces are strongly dependent on ionic strength [57,58].

Increasing ionic strength, the isotherm patterns remain unchanged (figures not reported), but while in soil TE there was no reduction in adsorption (expressed as % TW_{ads}), in soil EH and TH there was a reduction in the value of these parameters (Figure 5). The electrolyte ions, which are placed in the same plane as the outer-sphere complexes [59], compete with tungstate for the available soil surface sites subject to ionic-strength variations.

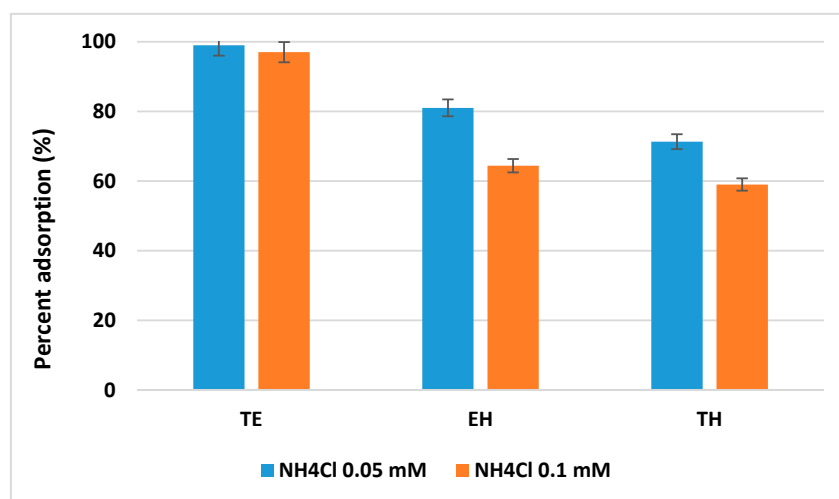


Figure 5. Percentage of the total amount of W adsorbed (TW_{ads}) at increasing ionic strengths for the three investigated soils.

The negligible effect of increasing ionic strength on adsorption in soil TE is indicative of the inner-sphere adsorption mechanism. In contrast, in soils EH and TH, adsorption appeared reduced by the increasing ionic strength, likely due to the anion competition with a consequent decrease in tungstate adsorption when the formation of outer-sphere complexes is involved [57].

Therefore, in soils EH and TH, tungstate adsorption proceeded through the formation of both inner- and outer-sphere complexes [55]. These results suggest the existence of different bonding strengths of tungstate ions in the three soils which are confirmed by the desorption experiments data which showed that tungstate is more loosely bound to adsorbing surfaces in soils EH and TH compared to soil TE. The simultaneous occurrence of inner- and outer-sphere complexes in the adsorption of WO_4^{2-} in soils are in accordance with results from studies conducted on other soils [20].

Distribution Coefficients

The affinity of tungstate to the soil surface was also reflected by the distribution coefficient K_d , which is defined as the ratio of adsorbed concentration to equilibrium concentration in soil solution. The distribution coefficient shows the ability of a soil to retain tungstate in the solid phase and the extent of its release into the soil solution. It is an essential parameter to determine the behaviour of substances in the soil environment in relation to bioavailability and leaching processes. The bioavailability and toxicity to organisms are essentially determined by the partitioning of tungsten between the solid and liquid phases of soil. Therefore, they are directly related to the distribution coefficients. A high value of K_d means that WO_4^{2-} is strongly adsorbed into the soil, while a low value means that it is highly mobile in soil. Figure 6 reports the K_d data for the three soils as a function of the equilibrium concentration in the adsorption process.

The K_d trends confirm the hypothesis that at low concentrations added tungstate ions are greatly adsorbed by soils presumably on sites characterized by a high affinity for this ion. The differences

in the K_d values between soil TE and the other two soils are very high, due to the differences in soil characteristics such as pH and organic matter. Increasing the concentration of WO_4^{2-} added, the adsorption proceeds on sites, characterized by a lower affinity for WO_4^{2-} with reduced differences in the K_d values among the three soils.

If K_d is examined with respect to the amount of tungstate desorbed the relationship between the amount desorbed and K_d was not linear, but fitted a quadratic equation better (Figure 7).

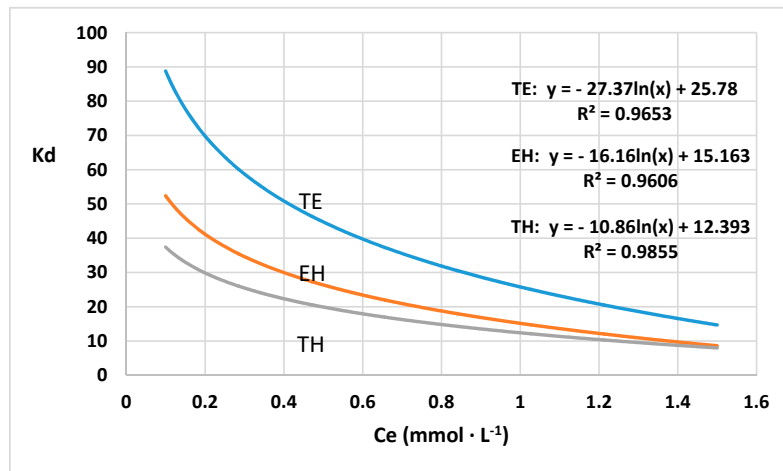


Figure 6. Patterns of K_d of the investigated soils versus equilibrium concentrations in the adsorption experiment.

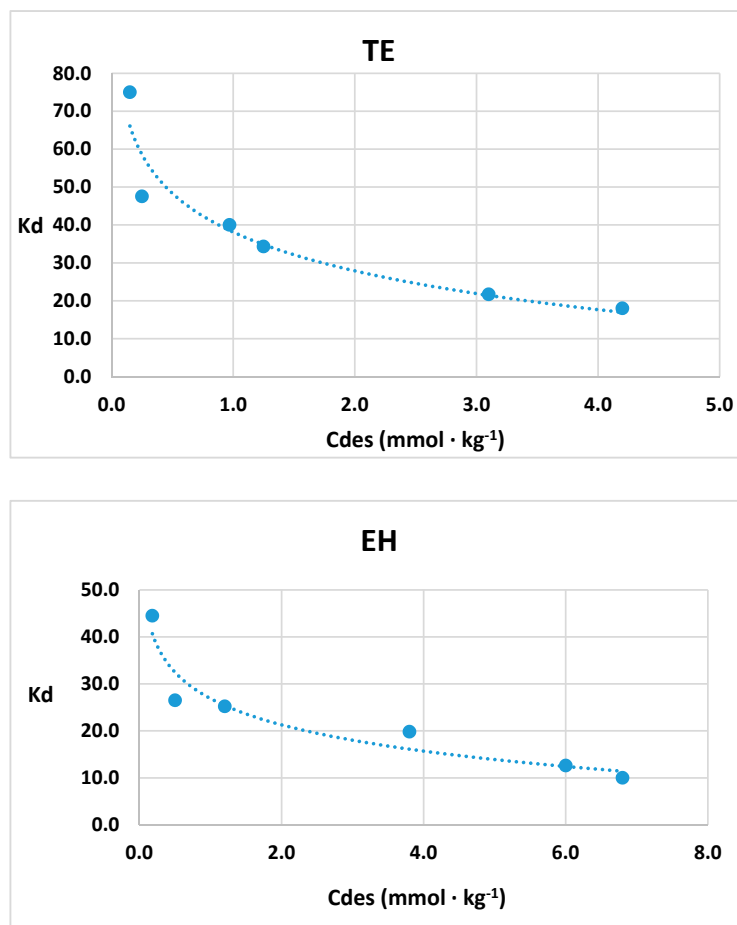


Figure 7. Cont.

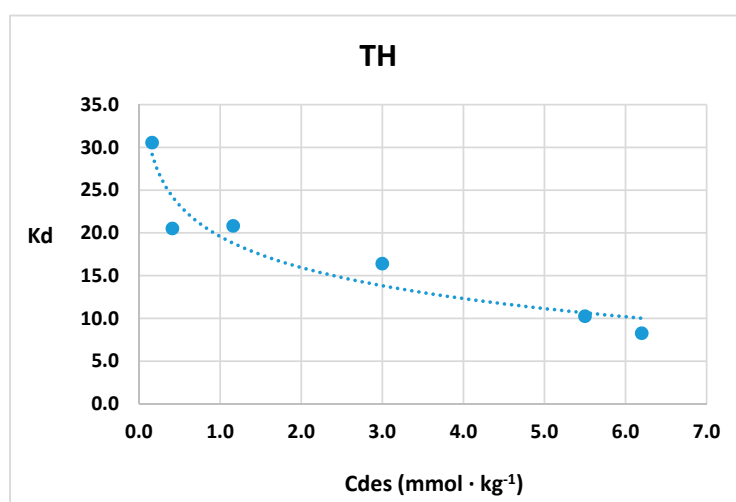


Figure 7. Trend of K_d vs. concentration of tungsten desorbed C_{des} .

Also, the non-linearity of the K_d trend can be ascribed to the existence of a tungstate fraction that once adsorbed onto soils is resistant to leaching, and which can be considered as nearly irreversibly adsorbed [60]. The K_d value is used in various environmental models to estimate the hazards deriving from a contaminant. Obviously, this parameter provides only indirect information on the type of surface interactions taking place because of the complexity of the adsorption/desorption mechanisms. For example, the desorption step can occur in the field in longer time with respect to laboratory experiments. However when the contact between tungstate ions and soil surfaces may have been months or years, the adsorbed fractions are characterized by higher strength of linkages and low bioavailability [50].

4. Conclusions

For Italian soils [26], there is little information available on the fate and transport of tungsten in Mediterranean soils, and there are no evaluation parameters for the concentration of tungsten in legislation concerning soil quality. No assessment has, therefore, been carried out regarding the potential risk for human exposure, despite the increasing concentrations of this element in the environment due to its increasing use in industrial activities. Relatively few studies have been carried out to investigate the adsorption and release of W from the soil in Mediterranean regions. In these soils the pH range most commonly encountered determines the presence of tungstate as dissociate ions together with polytungstates as the most abundant chemical species [35–37]. In these pH conditions, tungstate ion is considered as the only chemical form interacting with living cells, which utilize tungsten [61].

Adsorption/desorption is one of the most important processes affecting the mobility, and bioavailability of tungsten in the soil environment. As for Italian soils [26], we found a non-linear behaviour of tungstate sorption for the soils studied, which was likely due to the presence of multiple sites of sorption with different energies of retention. Our data show that there are two phases in the tungstate adsorption process in the three soils. In the first phase there is a specific adsorption characterized by strong bonds between the metal and the soil surfaces. In the second phase, weaker bonds are formed that lead to a greater release of tungsten in the desorption process. Tungstate anions initially link to the highest energy binding sites and then fill lower energy sites. As tungstate accumulates at binding sites, the soil surfaces become progressively negative, decreasing their affinity for this anion as tungstate concentrations increase. Thus in the desorption process, the release of tungstate is increased at higher tungstate concentrations due to the weaker linkages with soil surfaces.

Among the different characteristics of the soils examined, the adsorption and desorption processes are strictly dependent on the pH and organic matter content. Due to the unique features

of tungsten, it is hoped that this study will contribute to further research to drive risk-based decision-making. This particularly applies to contaminated soil, where preliminary studies [62] indicate that phytoremediation may be a potential treatment method since plants tend to accumulate tungsten in their tissues.

Author Contributions: Conceptualization, G.P. and F.P.; Writing—original draft, G.P. and F.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: Authors thank Irene Rosellini for technical assistance.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Koutsospyros, A.; Braidia, W.J.; Christodoulatos, C.; Dermatas, D.; Strigul, N.S. A review of tungsten: From environmental obscurity to scrutiny. *J. Hazard. Mater.* **2006**, *136*, 1–19. [[CrossRef](#)] [[PubMed](#)]
2. Shedd, K.B. Tungsten U.S. Geological Survey. *Miner. Commod. Summ.* **2011**, 176–177.
3. Oburger, E.; Vergar Cid, C.; Schwertberger, D.; Roschitz, C.; Wenzel, W.W. Response of tungsten (W) solubility and chemical fractionation to changes in soil pH and soil aging. *Sci. Total Environ.* **2020**, *731*, 139224. [[CrossRef](#)] [[PubMed](#)]
4. Seiler, R.L.; Stollenwerk, K.G.; Garbarino, J.R. Factors controlling tungsten concentrations in ground water, Carson Desert, Nevada. *Appl. Geochem.* **2005**, *20*, 423–441. [[CrossRef](#)]
5. Alvarez, M.A.; Galindo, P.J.; Perez, E.C. Molybdenum and tungsten complexes with carbon dioxide and ethylene ligands. *Chem. Sci.* **2019**, *10*, 8541–8546. [[CrossRef](#)]
6. Cui, M.; Mohajerin, T.J.; Adebayo, S.; Datta, S.; Johannesson, K.H. Investigation of tungstate thiolation reaction kinetics and sedimentary molybdenum/tungsten enrichments: Implication for tungsten speciation in sulfidic waters and possible applications for paleoredox studies. *Geochim. Cosmochim. Acta* **2020**, in press. [[CrossRef](#)]
7. Oburger, E.; Vergara Cid, C.; Preiner, J.; Hu, J.; Hann, S.; Wanek, W.; Richter, A. pH-Dependent Bioavailability, Speciation, and Phytotoxicity of Tungsten (W) in Soil Affect Growth and Molybdoenzyme Activity of Nodulated Soybeans. *Environ. Sci. Technol.* **2018**, *52*, 6146–6156. [[CrossRef](#)]
8. Kelly, A.D.R.; Lemaire, M.; Young, Y.K.; Eustache, J.H.; Guilbert, C.; Molina, M.F.; Mann, K.K. In vivo tungsten exposure alters B-cell development and increases DNA damage in murine bone marrow. *Toxicol. Sci.* **2013**, *131*, 434–446. [[CrossRef](#)]
9. Laulicht, F.; Brocato, J.; Cartularo, L.; Vaughan, J.; Wu, F.; Kluz, T.; Sun, H.; Oksuz, B.A.; Shen, S.; Peana, M.; et al. Tungsten-induced carcinogenesis in human bronchial epithelial cells. *Toxicol. Appl. Pharm.* **2015**, *288*, 33–39. [[CrossRef](#)]
10. Sheppard, P.R.; Ridenour, G.; Speakman, R.J.; Witten, M.L. Elevated tungsten and cobalt in airborne particulates in Fallon, Nevada: Possible implications for the childhood leukemia cluster. *Appl. Geochem.* **2006**, *21*, 152–165. [[CrossRef](#)]
11. Sheppard, P.R.; Speakman, R.J.; Ridenour, G.; Witten, M.I. Using lichen chemistry to assess airborne tungsten and cobalt in Fallon, Nevada. *Environ. Monit. Assess.* **2007**, *130*, 511–518. [[CrossRef](#)] [[PubMed](#)]
12. US EPA. *Technical Fact Sheet—Tungsten*; January 2014; EPA Office of Solid Waste and Emergency Response: Washington, DC, USA, 2014.
13. Clausen, J.L.; Korte, N. Environmental fate of tungsten from military use. *Sci. Total Environ.* **2009**, *407*, 2887–2893. [[CrossRef](#)] [[PubMed](#)]
14. US EPA. *Technical Fact Sheet Tungsten (5106P)*, EPA 505-F-17-004, 2017; Office of Land and Emergency Management: Washington, DC, USA, 2017.
15. Datta, S.; Vero, S.E.; Hettiarachchi, G.M.; Johannesson, K. Tungsten Contamination of Soils and Sediments: Current State of Science. *Curr. Pollut. Rep.* **2017**, *3*, 55–64. [[CrossRef](#)]
16. Kennedy, A.J.; Johnson, D.R.; Seiter, J.M.; Lindsay, J.H.; Boyd, R.E.; Bednar, A.J.; Allison, P.G. Tungsten toxicity, bioaccumulation, and compartmentalization into organisms representing two trophic levels. *Environ. Sci. Technol.* **2012**, *46*, 9646–9652. [[CrossRef](#)]

17. Koutsospyros, A.D.; Strigul, N.; Braidă, W.; Christodoulatos, C. Tungsten: Environmental pollution and health effects. In *Encyclopedia of Environmental Health*; Nriagu, J.O., Ed.; Elsevier: Burlington, VT, USA, 2011; pp. 418–426.
18. Gustafsson, J.P. Modelling molybdate and tungstate adsorption to ferrihydrite. *Chem. Geol.* **2003**, *200*, 105–115. [[CrossRef](#)]
19. Sen Tuna, G.; Braidă, W. Evaluation of the adsorption of mono- and poly- tungstates onto different types of clay minerals and Pahokee peat. *Soil Sediment. Contam.* **2014**, *23*, 838–849. [[CrossRef](#)]
20. Li, R.; Chunye, L.; Xitao, L. Adsorption of tungstate on kaolinite: Adsorption models and kinetics. *RSC Adv.* **2016**, *6*, 19872–19877.
21. Vissenberg, M.J.; Joosten, L.J.M.; Heffels, M.M.E.H.; van Welsenens, A.J.; de Beer, V.H.J.; van Santen, R.A. Tungstate versus Molybdate Adsorption on Oxidic Surfaces: A Chemical Approach. *J. Phys. Chem. B* **2000**, *104*, 8456–8461. [[CrossRef](#)]
22. Sun, J.; Bostick, B.C. Effects of tungstate polymerization on tungsten (VI) adsorption on ferrihydrite. *Chem. Geol.* **2015**, *417*, 21–31. [[CrossRef](#)]
23. Johannesson, K.H.; Dave, H.B.; Mohajerin, T.J.; Datta, S. Controls on tungsten concentrations in groundwater flow systems: The role of adsorption, aquifer sediment Fe(III) oxide/oxyhydroxide content, and thio tungstate formation. *Chem. Geol.* **2013**, *351*, 76–94. [[CrossRef](#)]
24. Hur, H.; Reeder, R.J. Tungstate sorption mechanisms on boehmite: Systematic uptake studies and X-ray absorption spectroscopy analysis. *J. Colloid. Interface Sci.* **2016**, *461*, 249–260. [[CrossRef](#)] [[PubMed](#)]
25. Rakshit, S.; Sallman, B.; Davantès, A.; Lefèvre, G. Tungstate (VI) sorption on hematite: An in situ ATR-FTIR probe on the mechanism. *Chemosphere* **2017**, *168*, 685–691. [[CrossRef](#)] [[PubMed](#)]
26. Petruzzelli, G.; Pedron, F. Tungstate adsorption onto Italian soils with different characteristics. *Environ. Monit. Assess.* **2017**, *189*, 379. [[CrossRef](#)] [[PubMed](#)]
27. Sparks, D.L. *Methods of Soil Analysis. Part 3. Chemical Methods*; Science Society of America Book Series: Madison, WI, USA, 1996; pp. 961–1010.
28. Klute, A. *Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. Agronomy Monograph No. 9*, 2nd ed.; American Society of Agronomy/Soil Science Society of America: Madison, WI, USA, 1986; pp. 383–411.
29. Dermatas, D.; Braidă, W.; Christodoulatos, C.; Strigul, N.; Panikov, N.; Los, M.; Larson, S. Solubility, sorption, and soil respiration effects of tungsten and tungsten alloys. *Environ. Forensics* **2004**, *5*, 5–13. [[CrossRef](#)]
30. Bednar, A.J.; Jones, W.T.; Chappell, M.A.; Johnson, D.R.; Ringelberg, D.B. A modified acid digestion procedure for extraction of tungsten from soil. *Talanta* **2010**, *80*, 1257–1263. [[CrossRef](#)]
31. Xie, X.; Chen, C.; Lu, X.; Luo, F.; Wang, C.; Alsaedi, A.; Hayat, T. Porous Ni Fe-oxide nanocubes derived from prussian blue analogue as efficient adsorbents for the removal of toxic metal ions and organic dyes. *J. Hazard. Mater.* **2019**, *379*, 120786. [[CrossRef](#)]
32. Usman, A. The relative adsorption selectivities of Pb, Cu, Zn, Cd and Ni by soils developed on shale in New Valley, Egypt. *Geoderma* **2008**, *144*, 334–343. [[CrossRef](#)]
33. Shaheen, S.M. Sorption and lability of cadmium and lead in different soils from Egypt and Greece. *Geoderma* **2009**, *153*, 61–68. [[CrossRef](#)]
34. Giles, C.H.; Smith, D.; Huitson, A. A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *J. Colloid. Interface Sci.* **1974**, *47*, 755–765. [[CrossRef](#)]
35. Bednar, A.J.; Boyd, R.E.; Jones, W.T.; McGrath, C.J.; Johnson, D.R.; Chappell, M.A.; Ringelberg, D.B. Investigations of tungsten mobility in soil using column tests. *Chemosphere* **2009**, *75*, 1049–1056. [[CrossRef](#)]
36. Davantès, A.; Costa, D.; Lefèvre, G. Infrared study of (poly) tungstate ions in solution and Sorbed into layered double hydroxides: Vibrational calculations and in situ analysis. *J. Phys. Chem.* **2015**, *119*, 12356–12364. [[CrossRef](#)]
37. Cruywagen, J.J. Protonation, oligomerization, and condensation reactions of vanadate (V), molybdate (VI), and tungstate (VI). In *Advances in Inorganic Chemistry*; Sykes, A.G., Ed.; Academic Press Inc.: San Diego, CA, USA, 2000; pp. 127–182.
38. Xu, N.; Christodoulatos, C.; Braidă, W. Modeling the competitive effect of phosphate, sulfate, silicate, and tungstate anions on the adsorption of molybdate onto goethite. *Chemosphere* **2006**, *64*, 1325–1333. [[CrossRef](#)] [[PubMed](#)]
39. Dixit, S.; Hering, J.G. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.* **2003**, *37*, 4182–4189. [[CrossRef](#)] [[PubMed](#)]

40. Sparks, D.L. *Environmental Soil Chemistry*; Academic Press: San Diego, CA, USA, 2003.
41. Elzinga, E.J.; Sparks, D.L. Phosphate adsorption onto hematite: An in situ ATR-FTIR investigation of the effects of pH and loading level on the mode of phosphate surface complexation. *J. Colloid. Interface Sci.* **2007**, *308*, 53–70. [[CrossRef](#)] [[PubMed](#)]
42. McBride, M.B. *Environmental Chemistry of Soils*; Oxford University Press: New York, NY, USA, 1994.
43. Karimian, N.; Johnston, S.G.; Burton, E.D. Antimony and arsenic behavior during Fe(II)-induced transformation of Jarosite. *Environ. Sci. Technol.* **2017**, *51*, 4259–4268. [[CrossRef](#)] [[PubMed](#)]
44. Karimian, N.; Johnston, S.G.; Burton, E.D. Antimony and arsenic partitioning during Fe²⁺-induced transformation of Jarosite under acidic conditions. *Chemosphere* **2018**, *195*, 515–523. [[CrossRef](#)] [[PubMed](#)]
45. Karimian, N.; Burton, E.D.; Johnston, S.G.; Hockmann, K.; Choppala, G. Humic acid impacts antimony partitioning and speciation during iron(II)-induced ferrihydrite transformation. *Sci. Total Environ.* **2019**, *683*, 399–410. [[CrossRef](#)]
46. Gecol, H.; Parfait, M.; Erdogan, E.; Sage, H. Biopolymer coated clay particles for the adsorption of tungsten from water. *Desalination* **2006**, *197*, 165–178. [[CrossRef](#)]
47. Holford, I.C.R.; Mattingly, G.E.G. A model for the behaviour of labile phosphate in soil. *Plant Soil* **1974**, *44*, 219–229. [[CrossRef](#)]
48. Barrow, N.J. A mechanistic model for describing the sorption and desorption of phosphate by soil. *Eur. J. Soil Sci.* **2015**, *66*, 9–18. [[CrossRef](#)]
49. Jing, Y.D.; He, Z.L.; Yang, X.E. Adsorption–Desorption Characteristics of Mercury in Paddy Soils of China. *J. Environ. Qual.* **2008**, *37*, 680–688. [[CrossRef](#)] [[PubMed](#)]
50. Alexander, M. Aging, Bioavailability, and Overestimation of Risk from Environmental Pollutants. *Environ. Sci. Technol.* **2000**, *34*, 4259–4265. [[CrossRef](#)]
51. Wenzel, W.W.; Kirchbaumer, N.; Prohaska, T.; Stingeder, G.; Lombi, E.; Adriano, D.C. Arsenic fractionation in soils using an improved sequential extraction procedure. *Anal. Chim. Acta* **2001**, *436*, 309–323. [[CrossRef](#)]
52. Khodaverdiloo, H.; Samadi, A. Batch equilibrium study on sorption, desorption, and immobilisation of cadmium in some semi-arid zone soils as affected by soil properties. *Soil Res.* **2011**, *49*, 444–454. [[CrossRef](#)]
53. Vega, F.A.; Covelo, E.F.; Andrade, M.L. Hysteresis in the individual and competitive sorption of cadmium, copper, and lead by various soil horizons. *J. Colloid. Interface Sci.* **2009**, *331*, 312–317. [[CrossRef](#)]
54. Rampoldi, E.A.; Hang, S.; Barriuso, E. Carbon-14-Glyphosate behavior in relationship to pedoclimatic conditions and crop sequence. *J. Environ. Qual.* **2014**, *43*, 558–567. [[CrossRef](#)]
55. Sander, M.; Lu, Y.; Pignatello, J.J. A thermodynamically based method to quantify true sorption hysteresis. *J. Environ. Qual.* **2005**, *34*, 1063–1072. [[CrossRef](#)]
56. Kashiwabara, T.; Takahashi, Y.; Marcus, M.A.; Uruga, T.; Tanida, H.; Terada, Y.; Usui, A. Tungsten species in natural ferromanganese oxides related to its different behavior from molybdenum in oxic ocean. *Geochim. Cosmochim. Acta* **2013**, *106*, 364–378. [[CrossRef](#)]
57. Wang, Y.; Tiwari, D.; Wang, H. Effect of ionic strength on adsorption of As(III) and As(V) on variable charge soils. *J. Environ. Sci.* **2009**, *21*, 927–932.
58. Kanematsu, M.; Young, T.M.; Fukushi, K.; Green, P.G.; Darby, J.L. Arsenic (III, V) adsorption on a goethite-based adsorbent in the presence of major co-existing ions: Modeling competitive adsorption consistent with spectroscopic and molecular evidence. *Geochim. Cosmochim. Acta* **2013**, *106*, 404–428. [[CrossRef](#)]
59. Hayes, K.F.; Papelis, C.; Leckie, J.O. Modeling ionic strength effects on anion adsorption at hydrous oxide/solution interfaces. *J. Colloid. Interface Sci.* **1988**, *125*, 717–726. [[CrossRef](#)]
60. Merrikhpour, H.; Jalali, M. Geostatistical assessment of solid–liquid distribution coefficients (K_d) for Cd, Cu, Pb and Zn in surface soils of Hamedan, Iran. *Model. Earth Syst. Environ.* **2015**, *1*, 2–9. [[CrossRef](#)]
61. Shanware, A.S.; Phadtare, P. Tungsten toxicity in soil and biological role of tungsten in bacteria. *Indian J. Sci.* **2014**, *10*, 36–42.
62. Erdemir, Ü.S.; Arslan, H.; Güleriyüz, G.; Güçer, Ş. Elemental Composition of Plant Species from an Abandoned Tungsten Mining Area: Are They Useful for Biogeochemical Exploration and/or Phytoremediation Purposes? *Bull. Environ. Contam. Tox.* **2017**, *98*, 299–303. [[CrossRef](#)] [[PubMed](#)]

