

Article

Adsorption/Desorption Patterns of Selenium for Acid and Alkaline Soils of Xerothermic Environments

Ioannis Zafeiriou, Dionisios Gasparatos  and Ioannis Massas *

Laboratory of Soil Science and Agricultural Chemistry, Agricultural University of Athens, 11855 Athens, Greece; j.zafeiriou@gmail.com (I.Z.); gasparatos@aua.gr (D.G.)

* Correspondence: massas@aua.gr

Received: 22 July 2020; Accepted: 23 September 2020; Published: 24 September 2020



Abstract: Selenium adsorption/desorption behavior was examined for eight Greek top soils with different properties, aiming to describe the geochemistry of the elements in the selected soils in terms of bioavailability and contamination risk by leaching. Four soils were acid and four alkaline, and metal oxides content greatly differed between the two groups of soils. The concentrations of Se(IV) used for the performed adsorption batch experiments ranged from 1 to 50 mg/L, while the soil to solution ratio was 1 g/0.03 L. Acid soils adsorbed significantly higher amounts of the added Se(IV) than alkaline soils. Freundlich and Langmuir equations adequately described the adsorption of Se(IV) in the studied soils, and the parameters of both isotherms significantly correlated with soil properties. In particular, both K_F and q_m values significantly positively correlated with ammonium oxalate extractable Fe and with dithionite extractable Al and Mn, suggesting that amorphous Fe oxides and Al and Mn oxides greatly affect exogenous Se(IV) adsorption in the eight soils. These two parameters were also significantly negatively correlated with soil electrical conductivity (EC) values, indicating that increased soluble salts concentration suppresses Se(IV) adsorption. No significant relation between adsorbed Se(IV) and soil organic content was recorded. A weak salt (0.25 M KCl) was used at the same soil to solution ratio to extract the amount of the adsorbed Se(IV) that is easily exchangeable and thus highly available in the soil ecosystem. A much higher Se(IV) desorption from alkaline soils was observed, pointing to the stronger retention of added Se(IV) by the acid soils. This result implies that in acid soils surface complexes on metal oxides may have been formed restricting Se desorption.

Keywords: selenium; acid soils; alkaline soils; adsorption; desorption; Freundlich; Langmuir; Mediterranean soils

1. Introduction

Selenium (Se) is an essential micronutrient for humans and animals, but can lead to toxicity when taken in excessive amounts. Plants are the main source of dietary Se, but the essentiality of Se for plants is still controversial, although the beneficial effects of low doses of Se on plants have been reported in several studies [1–3]. The concentration of Se in plants is directly related to the concentration and the bioavailability of the element in the soil and the plant species [4]. Selenium reactivity in soils depends not only on its total content but also on its chemical form [5,6]. The mobility and plant-availability of Se in soil is controlled by numerous chemical and biochemical processes, as follows: sorption, desorption, microbial activity, the formation of organic and inorganic complexes, precipitation, and dissolution and methylation to volatile compounds [6,7]. Depending on the oxidation state, Se is present in soil as selenide (Se_2^-), elemental selenium (Se^0), selenite (SeO_3^{2-}), selenate (SeO_4^{2-}) and organic Se. The main factors controlling Se solubility and availability in soils are considered to be pH, oxidation-reduction potential (Eh), metallic oxy-hydroxides and clays, organic matter, microorganisms, and the presence

of competing ions [6,8]. Comprehensive information regarding Se geochemistry and Se behavior in soil–plant systems is included in the extensive reviews of Winkel et al. [6], Etteieb et al. [8] and Schivaon et al. [9]

The total concentration of Se in soils varies spatially, and the average global value is quite low at 0.4 mg kg^{-1} , ranging between 0.01 and 2 mg kg^{-1} [9,10]; soils containing less than 0.5 mg kg^{-1} Se are considered as deficient. In humans, Se deficiency occurs when a dietary intake of Se is $<40 \text{ }\mu\text{g/day}$ and chronic toxicity is observed above levels of $>400 \text{ }\mu\text{g/day}$ [11]. WHO has recommended $50\text{--}55 \text{ }\mu\text{g/day}$ Se in human diet [12–14]. It has been estimated that more than 1 billion people all over the world are suffering Se malnutrition, which makes them susceptible to health problems such as growth retardation, impaired bone metabolism and abnormalities in thyroid function [7,9,12]. Selenium deficiency has been reported in countries such as Canada, China, Scotland, Japan, New Zealand, Spain and USA [6,7,15,16]. Thus, numerous studies have been carried out aiming to enrich agricultural products with Se [17–19], and to examine the behavior of added Se in soils. Greece is also considered as an Se deficient area (daily Se intake $<55 \text{ }\mu\text{g}$) [20], and very low selenium concentrations were recorded in Greek agricultural products such as soft and hard wheat, barley, oat, rye and corn [21]. However, published studies reporting on Se concentrations or describing the geochemical behavior of the element in Greek soils are missing from the literature. Considering that Greek soils are Se deficient, it is highly possible that in the future Se addition by fertilization can be proposed in order to enrich edible agricultural products. Thus, the geochemical behavior of Se in soils with different physicochemical properties should be examined to ensure the availability of Se for plant uptake and to restrict Se leaching. It is worth to note that Greek soils can be regarded as representative of Mediterranean soils, and any information on the geochemistry of Se in these soils can be projected and used for soils of similar characteristics formed and developed under comparable environmental conditions.

The purpose of the present study was to obtain data on the behavior of freshly added Se(IV) in acid and alkaline Greek soils with different physicochemical properties, and to evaluate the potential environmental risks arising from Se(IV) application. Thus, a batch experiment was conducted to investigate (a) the adsorption of different Se(IV) concentrations in the selected soils, (b) the desorption patterns of sorbed Se(IV) by using 0.25 M KCl as a desorbing agent, as well as (c) to determine the soil properties that mainly affect the sorption/desorption processes.

2. Materials and Methods

2.1. Soils

Eight composite top soil samples (0–20 cm) representing a range of different physicochemical properties were collected from arable lands of Peloponnese (Greece) and used in this study. The main criterion for the selection of sampling sites was the soil pH. Four of the soils were acid and four alkaline. The samples were transferred in sterile sampling bags to the laboratory, air-dried, crushed, passed through a 2-mm sieve and finally stored again in sterile sampling bags. Particle size distribution was determined by the hydrometer method [22], while pH and EC were measured in a 1:1 (w/v) soil/water ratio [23]. Total carbonates content (CaCO_3) was calculated by measuring the evolved CO_2 following HCl dissolution [24]. The Loeppert and Suarez [25] ammonium oxalate method was used in order to determine active carbonate fraction. Available phosphorous (*p*) was obtained by using the Olsen method [26] and organic carbon (OC) content was determined by the Walkley-Black's protocol [27]. Amorphous and free Fe, Mn and Al oxide contents were calculated by the ammonium oxalate buffer methods [28] and by the sodium–bicarbonate–dithionate (CBD) [29], respectively. Total Se was extracted by aqua regia [30].

2.2. Stock Solutions and Reagents

Stock solutions containing 1, 10, 20, 30, 40 and $50 \text{ mg Se(IV) L}^{-1}$ were prepared by diluting the appropriate amount of SeO_2 in deionized water and were stored in airtight sterile glass containers.

The desorbing solution of 0.25 M KCl was prepared by dissolving the proper amount of KCl salt in deionized water. This solution was also stored in airtight sterile glass containers.

2.3. Batch Experiments

For every soil six falcon tubes were used. One gram of soil was introduced to each falcon tube and 30 mL of the appropriate stock solution was added, resulting in a 1:30 w/v soil:solution ratio. Afterwards the falcon tubes were placed in an incubator with an adjusted steady temperature of 22 ± 1 °C and gently shaken at 120 rpm for 24 h on an end-to-end shaker. Then, the falcon tubes were centrifuged for 5 min at 3500 rpm and the supernatants were filtered through a Whatman paper No 42. Absorbed Se(IV) was calculated by the difference between the initial and the equilibrium solutions Se(IV) concentrations. Moreover, since pH plays an important role in Se behavior in the soil environment, the pH values of the initial Se(IV) solutions and of the equilibrium solutions were also recorded.

To desorb adsorbed Se(IV), 30 mL of 0.25 M KCl extractant solution was added in the falcon tubes containing the soil samples. Falcon tubes were placed again in an incubator with an adjusted steady temperature of 22 ± 1 °C, and gently shaken at 120 rpm for 24 h on an end-to-end shaker, centrifuged, and filtered through a Whatman paper No. 42, following the same procedure as described above. Desorbed Se(IV) was determined in the equilibrium solutions at the end of the process.

2.4. Isotherm Equations

Langmuir and Freundlich adsorption isotherms were produced based on the equilibrium adsorption data. However, the Langmuir model assumes that biosorption takes place at specific homogeneous sites on the adsorbent by monolayer coverage, while the Freundlich model is empirical and assumes sorption on a heterogeneous surface.

The linear form of the Langmuir model is [31]

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{b_L q_m} \quad (1)$$

where C_e is the equilibrium concentration of ion in the solution (mg/L), q_e is the amount of ion adsorbed per gram of adsorbent at equilibrium (mg/g), q_m is the monolayer biosorption capacity (mg/g) and b_L is the affinity constant related to the binding strength of adsorption (L/mg). The values of q_m and b_L can be determined from the linear plot of C_e/q_e versus C_e .

The linear form of the Freundlich model is [32]

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where C_e is the equilibrium concentration of ion in the solution (mg/L), q_e is the amount of ion adsorbed per gram of adsorbent at equilibrium (mg/g), K_F is a constant relating to the biosorption capacity (mg/g) (L/mg)^{1/n} and $1/n$ is an empirical parameter relating to the biosorption intensity. The values of K_F and $1/n$ can be determined by plotting $\ln q_e$ versus $\ln C_e$.

2.5. Distribution Coefficient (K_d)

The distribution coefficient (K_d) (L/kg) was calculated according to the following formula:

$$K_d = q_e/C_e \quad (3)$$

where C_e is the equilibrium concentration of ion in the solution (mg/L) and q_e is the amount of ion adsorbed per kg of adsorbent at equilibrium (mg/kg).

2.6. Analytical Determinations

Selenium, iron, manganese and aluminum concentrations were determined by using an atomic absorption spectrophotometry, Varian—spectraAA-300system. For the determination of Se at low concentrations, a Varian model VGA77 hydride generator was used. Available phosphorus concentrations were determined by a Shimadzu UV-1700 spectrophotometer. Every 10 samples a control sample was analyzed, and at the end of the measurements procedure 30% of the samples were reanalyzed to test reproducibility.

2.7. Statistics

Correlation and *t*-test analysis ($p < 0.05$) were performed using STATISTICA 10 software (StatSoft Inc., Tulsa, 74104 OK, USA).

3. Results

3.1. Soil Properties

The physicochemical properties of the studied soils and the total Se concentrations are summarized in Table 1. Most of the soils are characterized as medium to fine textured with low organic carbon content, as expected for Mediterranean agricultural soils, and with very low total Se concentrations, less than 0.28 mg kg^{-1} , pointing to Se deficiency [33]. Ammonium oxalate and dithionite extractable Fe, Al and Mn are expressed as % oxides content ($\text{g } 100 \text{ g}^{-1}$ soil) and presented as Fe_o, Al_o, Mn_o and Fe_d, Al_d and Mn_d, respectively. Metal oxide concentrations greatly varied, ranging between 0.08 and 0.40% and 0.72 and 6.32% for Fe_o and Fe_d, between 0.55 and 1.03% and 0.06 and 0.26% for Al_o and Al_d and between 0.01 and 0.10% and 0.02 and 0.15% for Mn_o and Mn_d. The pH range of both alkaline and acid soils was very narrow—7.4 to 7.8 for alkaline soils and 5.5 to 6.0 for acid soils. Electrical conductivity values in the alkaline soils were significantly higher than in the acid soils ($p < 0.001$, $n = 4$), but were not restrictive for the growth of crops. Most soils were marginally to moderately supplied with available phosphorus.

Table 1. Soil physicochemical characteristics.

Soil properties	Alkaline Soils					Acid Soils		
	1	2	3	4	5	6	7	8
Clay (%)	37.6	23.6	17	28.7	24.7	32.4	16.4	30.1
Silt (%)	25.7	32	18	30.3	26.3	24.3	20.3	20.3
Sand (%)	36.7	44.4	65	41	49	43.3	63.3	49.6
Texture	CL	CL	SL	CL	SCL	CL	SL	SCL
pH (1:1)	7.45	7.42	7.44	7.76	5.49	5.88	6.01	5.8
CaCO ₃ eq. (%)	4.5	4.55	18.7	16.3	<D.L. *	<D.L.	<D.L.	<D.L.
Act. CaCO ₃ (%)	3.13	2.63	0.5	4.86	<D.L.	<D.L.	<D.L.	<D.L.
EC ($\mu\text{S}/\text{cm}$)	1900	1365	1545	1750	960	625	475	400
Organic Carbon %	1.05	0.95	1.50	0.70	1.55	0.80	0.75	0.85
Fe _d (%)	1.8	0.73	6.32	1.57	2.26	3.22	2.33	1.28
Fe _o (%)	0.2	0.13	0.13	0.08	0.17	0.4	0.31	0.35
Al _d (%)	0.12	0.06	0.06	0.12	0.13	0.26	0.16	0.22
Fe _o /Fe _d	0.11	0.18	0.02	0.05	0.08	0.12	0.13	0.27
Al _o (%)	0.9	0.64	0.55	0.66	0.9	1.02	0.46	1.03
Mn _d (%)	0.05	0.04	0.03	0.02	0.09	0.1	0.07	0.15
Mn _o (%)	0.04	0.04	0.02	0.02	0.08	0.1	0.05	0.06
Se total (mg kg^{-1})	0.21	0.28	0.07	0.06	0.16	0.08	0.18	0.05
p Olsen. (mg kg^{-1})	4	18.8	8.8	6.3	11.7	10.6	27.6	6.4

* D.L.: Detection Limit.

3.2. Selenium Adsorption

Acid soils showed a much higher retention of added Se(IV) than alkaline soils, in accordance with many studies [6,34–36]. In particular, Se(IV) adsorption ranged between 8.52 and 234 mg kg^{-1}

(Figure 1a) for alkaline soils, while the corresponding range for acid soils was 19.2–558.9 mg kg⁻¹ (Figure 1b).

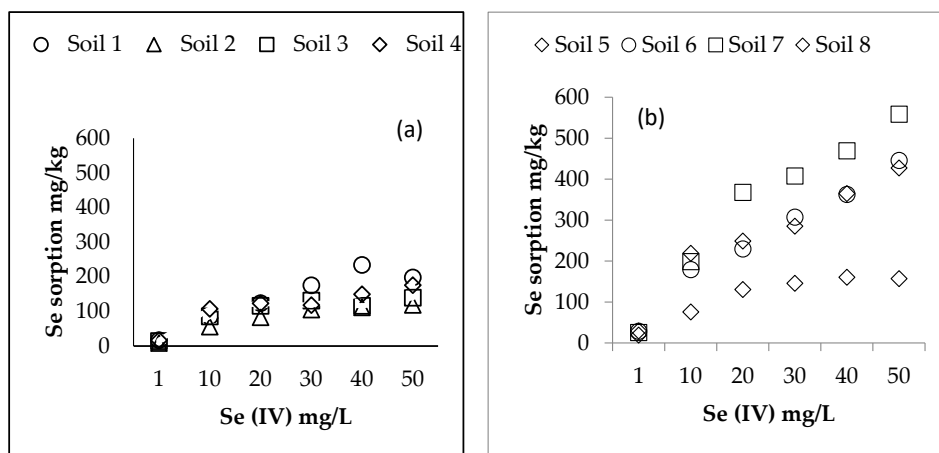


Figure 1. Se(IV) sorption on the studied soils (a) alkaline and (b) acid. Contact time 24 h, agitation rate 125 rpm, sorbent/solution ratio 1 g/0.03 L, Se(IV) concentrations at start time from 1 to 50 mg/L, temperature 22 °C.

The distribution coefficient (K_d) is a measure of the occupation of available sorption sites in relation to the concentration of the added element. Depending on added Se(IV) concentrations, the Se(IV) K_d values were within the ranges 2.6–36.7 and 3.5–1091.5 L/kg for alkaline and acid soils, respectively. Over the whole range of added Se(IV) concentrations, the K_d values of acid soils were considerably higher than those of the alkaline soils (Figure 2). The observed K_d values for the acid soils were noticeably higher than those reported by Soderlund et al. [36] for selenite adsorption on mineral soils (0.4–240 L/kg), while the highest K_d values are close to those determined by Sheppard et al. [37] for indigenous selenium (800–1500 L/kg). A decreasing trend of K_d values is commonly observed as the concentration of the element in solution increases, indicating that proportionally less of the added element is adsorbed by the soil colloids. Indeed, for all studied soils, K_d decreased as the Se(IV) solution concentration increased (Figure 2), and the higher to lower K_d ratio ranged between 4.6 and 9.1 for alkaline soils, whereas the corresponding range for acid soils was 10–90.2.

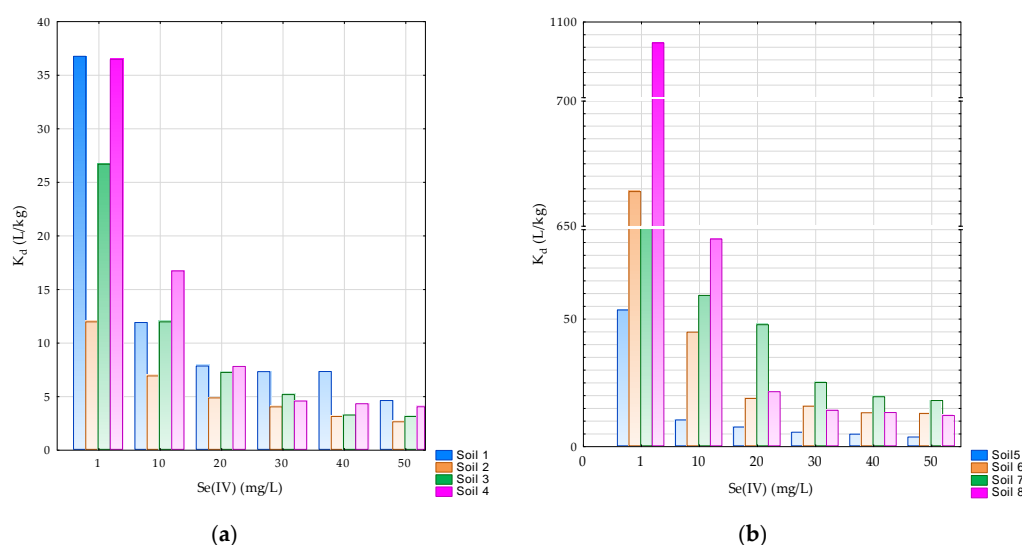


Figure 2. Values of Se(IV) K_d (L/kg) for the studied soils (a) alkaline and (b) acid. Contact time 24 h, agitation rate 125 rpm, sorbent/solution ratio 1 g/0.03 L, Se(IV) concentrations at start time from 1 to 50 mg/L, temperature 22 °C.

3.3. Selenium Desorption

In the present study, 0.25 M KCl was used to extract adsorbed Se(IV). As is stated by Dhillon and Dhillon [34] and Zhu et al. [38], chloride ion can replace non-specifically adsorbed Se through ion exchange and mass action mechanisms. The desorption pattern was almost identical for all soils, i.e., increasing the initial Se(IV) solution concentration resulted in increasing the Se amounts desorbed from the soils (Figure 3). For all initial Se(IV) concentrations, less Se desorbed from acid soils, a trend more pronounced for initial solution concentrations up to 40 mg Se(IV)/L. Depending on the initial Se(IV) solution concentration, desorbed Se ranged between 2.6 and 117.6 and 0.2 and 84 mg kg⁻¹ for alkaline and acid soils respectively (Figure 3).

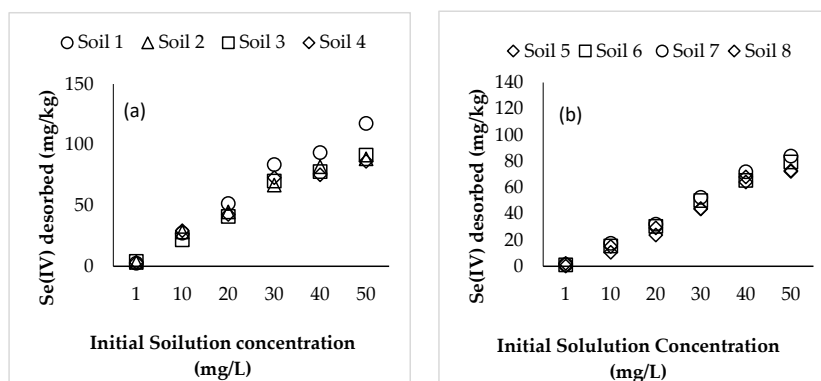


Figure 3. Se(IV) desorption from the studied soils (a) alkaline and (b) acid. Contact time 24 h, agitation rate 125 rpm, sorbent/solution ratio 1 g/0.03 L, temperature 22 °C.

3.4. Equilibrium Solutions pH

For all soils the acid initial solutions, pH led to acidic equilibrium solutions pH (Figure 4). In particular, the equilibrium solutions’ pH values for alkaline soils showed a decrease between one and three units as the concentration of added Se(IV) increased, while for acid soils the corresponding decrease was sharp for a 10 mg/L initial Se(IV) concentration, remaining almost constant thereafter for higher Se(IV) concentrations. Alkaline soils 3 and 4 showed higher resistances to pH changes than alkaline soils 1 and 2, probably due to the higher buffering capacity attributed to the higher carbonates content (Table 1).

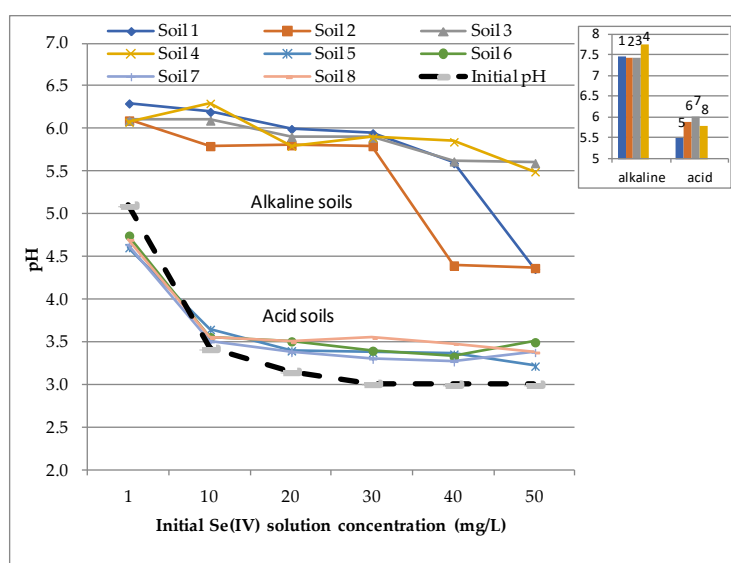


Figure 4. Equilibrium solutions pH values. Dashed line shows the initial solutions pH values. Soil pH values are presented in the incorporated frame.

4. Discussion

4.1. Selenium Adsorption

The experimental data fitted well with Freundlich and Langmuir isotherms, in agreement with Dhillon and Dhillon's results [35] (Table 2). The calculated adsorption maxima (q_m) from the Langmuir isotherm were higher for acid soils, as was in most cases the value of the bonding constant (b_L), indicating the stronger Se(IV) retention by the acid soils.

Table 2. Parameters of the Langmuir and Freundlich models for Se(IV) sorption in the eight soils. Contact time 24 h, agitation rate 125 rpm, sorbent/solution ratio 1 g/0.03 L, Se(IV) concentrations at start time from 1 to 50 mg/L, temperature 22 °C.

Soil	Langmuir Constants				Freundlich Constants			
	q_m (mg/g)	b_L (L/mg)	R^2	p -Value	K_F (mg/g) (L/mg) ^{1/n}	1/n	R^2	p -Value
1	0.26	0.085	0.9	<0.01	4.16	0.578	0.987	<0.001
2	0.15	0.076	0.996	<0.001	2.93	0.648	0.980	<0.001
3	0.15	0.203	0.979	<0.001	3.90	0.514	0.939	<0.01
4	0.18	0.152	0.939	<0.01	4.29	0.492	0.935	<0.01
5	0.18	0.140	0.973	<0.001	4.26	0.458	0.991	<0.001
6	0.46	0.157	0.894	<0.01	7.33	0.394	0.993	<0.001
7	0.61	0.176	0.969	<0.001	6.95	0.571	0.979	<0.001
8	0.42	0.246	0.921	<0.01	7.83	0.355	0.973	<0.001

The parameters of both isotherms, i.e., K_F and $1/n$ from the Freundlich isotherm, and q_m and b_L from the Langmuir isotherm, showed significant correlations with soil constituents. Both K_F and q_m significantly positively correlated with ammonium oxalate extractable Fe and with dithionite extractable Al and Mn ($p < 0.01$, Table 3), underpinning the crucial role of amorphous Fe, Al and Mn oxides in the exogenous Se(IV) behavior of the studied soils. The ability of Fe (especially amorphous), Al and Mn oxides to control Se geochemical behavior has been highlighted in many studies, supporting thus the leading significance of metal oxides in regulating Se mobility in soils [6,10,34,39–41]. K_F and q_m were also significantly negatively correlated with EC ($p < 0.05$, Table 3) and negatively but not significantly with bonding constant (b_L). These relations suggest that an increased soluble salts concentration suppresses both Se(IV) adsorption and strength of Se(IV) retention in soils, and leads to the increased availability of freshly added Se(IV) in the soil environment. This finding is also reported in the review of Natacha et al. [10] and in references therein. Furthermore, the bonding constant (b_L) of the Langmuir isotherm significantly positively correlated with the Fe_o/Fe_d values of acid soils and with the eqCaCO₃ content of alkaline soils (Table 3), pointing to the fact that in acid soils the fresh Se(IV) retention strength increases when amorphous Fe oxides constitute a larger part of free the Fe oxides, whereas in alkaline soils carbonates may possibly affect Se(IV) sorption. No significant correlation between the organic matter content and the initial or the adsorbed Se(IV) content was observed, a conclusion commonly reached by many researchers. Coppin et al. [42] did not find a direct relation between adsorbed Se and organic material, and suggest that Se may be indirectly sorbed on organic particles by forming associations with surface Fe oxides and clays. Additionally, Soderlund et al. [36] reported the limited importance of organic matter on Se retention compared to Fe and Al phases, even when the latter are incorporated in organic substances. Though clay is considered to affect Se sorption in soils [6,43], no significant correlations emerged between the clay content of the soils and the parameters of the Langmuir and Freundlich isotherms, or the distribution coefficient.

In Table 3, the correlation coefficients for Fe_o, Ald and Mnd and mean K_d (calculated from K_d values for each initial added Se concentration) relations are presented. The significant correlations between K_d values, ammonium oxalate extractable Fe and dithionite extractable Al and Mn ($p < 0.05$) further support that metal oxides govern Se(IV) sorption in the studied soils. The point of zero charge (PZC) of most Fe-oxides was shown to deviate slightly, ranging usually between pH 7 and 9, while the

pH_{pzc} values for various Al oxides reported in the literature vary widely, with a median of 8.6. [44,45]. In the pH range of equilibrium solutions, the Fe and Al oxides are positively charged and can adsorb negatively charged Se species. At low pH values, Mn oxides may have offered additional positively charged sites, since the PZC for most Mn oxides usually occurs at $pH < 5$ [46,47], leading to the increased adsorption capacity of acid soils. Nakamaru et al. [48], by using ^{75}Se as a tracer, found that the K_d values for selenite adsorption in Japanese soils were highly correlated with the active Al (Al_d) and Fe(Fe_o) content of the soils. Premarantha et al. [49] reached the same conclusion for acid soils from rice-growing areas in Sri Lanka. However, Zhe Li et al. [50] did not observe any significant relation between K_d and Al_o and/or Fe_o concentrations in 18 soils from China, and report only a strong negative correlation between K_d and soil pH values, indicating the stronger adsorption of selenite in acid soils. According to Table 3, the EC of soils was also significantly negatively correlated with mean K_d values ($p < 0.05$). Interestingly, Se availability was not only regulated by the absolute poorly crystallized iron oxides, but also by the relative Fe_o content in the free iron oxides, as can be deduced from the significant correlation between mean K_d and Fe_o/Fe_d values ($p < 0.05$, Table 3). Considering that the Fe_o/Fe_d ratio is used as an indicator for soil development, this result leads to the speculation that the stage of soil development can influence added Se(IV) behavior in the soil environment, and ultimately in the food chain. Nevertheless, the soils of the present study may have been formed from different parent materials, and such observations could be case specific, but may also be regarded as an indication for further research.

Table 3. Correlation coefficients, significant at $p < 0.05$ except q_m -Mnd and b_L -EC pairs (in italics) ($n = 8$).

Variables	Fe_o	Al_d	Mn_d	Fe_o/Fe_d	EC	$\text{eqCaCO}_3\%$
K_F	0.91	0.91	0.80		−0.83	
q_m	0.86	0.75	<i>0.59</i>		−0.77	
b_L				0.99 ($n = 4$)	−0.57	0.96 ($n = 4$)
Mean K_d	0.79	0.85	0.89	0.75		
Mean Se desorption %	−0.86	−0.88	−0.80			

4.2. Selenium Desorption

Selenium desorption, presented as the percentage of the adsorbed Se(IV) concentration found in the equilibrium desorption solutions, increased as the added Se(IV) amounts increased (Figure 5). Much lower Se% desorption from the acid than from the alkaline soils was observed, indicating a stronger retention of fresh Se(IV) by the acid soils. In fact, the mean Se% desorption (the average of Se% values for each initial added Se concentration) from the acid soils was significantly lower than the mean Se% desorption from alkaline soils ($p < 0.01$). Acid soils provided more active sites for the adsorption of negatively charged Se(IV) forms, since when lowering the pH positive charges on soil colloids increase, i.e., there is a higher protonation of surface hydroxyl groups, such as Fe-OH and Al-OH functional groups [36]. However, the stronger retention of Se(IV) by acid soils over the whole concentration range implies the involvement of different sorption mechanisms by the two groups of soils. It is probable that surface complexes may have been formed between Se(IV) species and oxides that lowered the reversibility of sorption process in acid soils. As is shown in Figure 4, for acid soils the pH of equilibrating solutions was very low, supporting the claim that stronger acidic conditions may have occurred close to the surfaces of active soil colloids that could lead to the formation of Se species preferably sorbed on such sites [6,10,40]. On the contrary, Se on the active surfaces of alkaline soils may have been retained mostly as easily exchangeable, thus leading to higher Se desorption by KCl. Numerous studies support the claim that low soil pH favors the higher sorption of Se (independently of Se speciation in equilibrating solutions) [8,51–53] but much less has been done on the evaluation of freshly added Se(IV)'s desorption behavior in acid and alkaline soils. The dominant role of metal oxides in the sorption–desorption behavior of Se(IV) under the conditions of the performed batch

experiments is also supported by the significant negative correlations between mean Se% desorption values and oxides concentrations (Table 3).

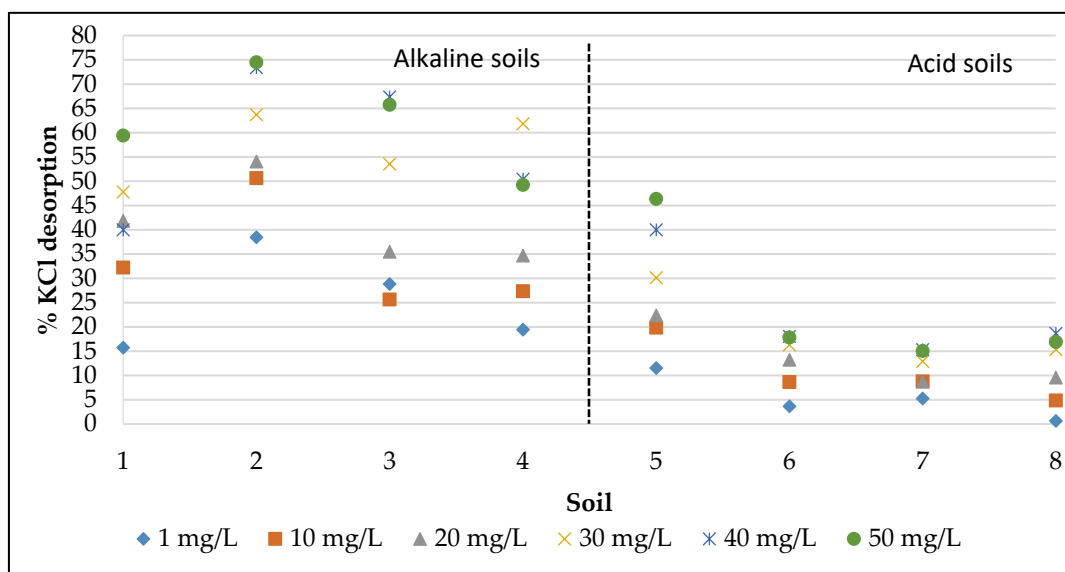


Figure 5. Percentage Se desorption by 0.25 M KCl from alkaline and acid soils. Contact time 24 h, agitation rate 125 rpm, sorbent/solution ratio 1 g/0.03 L, temperature 22 °C.

5. Conclusions

Both the adsorption and desorption processes of freshly added Se(IV) in acid and alkaline soils revealed distinct differences between the two groups of soils. Acid soils adsorbed significantly higher amounts of added Se(IV) than alkaline soils, and alkaline soils desorbed more Se. Fe, Al and Mn oxides, and particularly amorphous Fe oxides content, were the key parameters controlling the sorption/desorption of Se(IV) in the studied soils. Indeed, increased Fe_o concentration led to higher Se(IV) sorption and to lower Se desorption from the studied soils. Soil pH and the equilibrium solutions' pH strongly influenced both sorption and desorption patterns, providing more positively charged sites on oxides surfaces, leading to higher Se(IV) sorption. Furthermore, metal oxide chemistry at low pH values favored the formation of stronger surface complexes, thus suppressing the Se desorption from acid soils by a weak salt. Overall, the results of this study showed that metal oxides content and pH determine Se geochemistry in soils. Considering that biofortification through plant uptake is also crop/plant-dependent, Se(IV) application in agricultural soils should be site-specific, since a high Se leaching hazard in alkaline soils with low metal oxides concentration may emerge, and low Se availability in acid soils with high metal oxides contents can appear.

Author Contributions: I.Z.: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing—original draft. D.G.: Methodology, Validation, Resources, Data curation, Writing—review and editing. I.M.: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing—original draft, Writing—review and editing, Visualization, Supervision, Project administration. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

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

References

- Cartes, P.; Jara, A.A.; Pinilla, L.; Rosas, A.; Mora, M.L. Selenium improves the antioxidant ability against aluminium-induced oxidative stress in ryegrass roots. *Ann. Appl. Biol.* **2010**, *156*, 297–307. [[CrossRef](#)]
- Hasanuzzaman, M.; Fujita, M. Selenium Pretreatment Upregulates the Antioxidant Defense and Methylglyoxal Detoxification System and Confers Enhanced Tolerance to Drought Stress in Rapeseed Seedlings. *Biol. Trace Elem. Res.* **2011**, *143*, 1758–1776. [[CrossRef](#)] [[PubMed](#)]

3. Gupta, S.; Gupta, M. Alleviation of selenium toxicity in *Brassica juncea* L.: Salicylic acid-mediated modulation in toxicity indicators, stress modulators, and sulfur-related gene transcripts. *Protoplasma* **2016**, *253*, 1515–1528. [[CrossRef](#)]
4. Dinh, Q.; Wang, M.; Tran, T.; Zhou, F.; Wang, D.; Zhai, H. Bioavailability of selenium in soil-plant system and a regulatory approach. *Crit. Rev. Environ. Sci. Technol.* **2018**, *49*, 443–517. [[CrossRef](#)]
5. Finley, J.W.; Davis, C.D.; Feng, Y. Selenium from high selenium broccoli protects rats from colon cancer. *J. Nutr.* **2000**, *130*, 2384–2389. [[CrossRef](#)]
6. Winkel, L.; Vriens, B.; Jones, G.; Schneider, L.; Pilon-Smits, E.; Bañuelos, G. Selenium Cycling across Soil-Plant-Atmosphere Interfaces: A Critical Review. *Nutrients* **2015**, *7*, 4199–4239. [[CrossRef](#)]
7. Hartikainen, H. Biogeochemistry of selenium and its impact on food chain quality and human health. *J. Trace Elem. Med. Biol.* **2005**, *18*, 309–318. [[CrossRef](#)]
8. Etteieb, S.; Magdouli, S.; Zolfaghari, M.; Brar, S. Monitoring and analysis of selenium as an emerging contaminant in mining industry: A critical review. *Sci. Total Environ.* **2020**, *698*, 134339. [[CrossRef](#)]
9. Schiavon, M.; Nardi, S.; dalla Vecchia, F.; Ertani, A. Selenium biofortification in the 21st century: Status and challenges for healthy human nutrition. *Plant Soil* **2020**. [[CrossRef](#)]
10. Natasha Shahid, M.; Niazi, N.K.; Khalid, S.; Murtaza, B.; Bibi, I.; Rashid, M.I. A critical review of selenium biogeochemical behavior in soil-plant system with an inference to human health. *Environ. Pollut.* **2018**, *234*, 915–934. [[CrossRef](#)]
11. Winkel, L.H.; Johnson, C.A.; Lenz, M.; Grundl, T.; Leupin, O.X.; Amini, M.; Charlet, L. Environmental selenium research: From microscopic processes to global understanding. *Environ. Sci. Technol.* **2011**, *46*, 571–579. [[CrossRef](#)] [[PubMed](#)]
12. World Health Organization (WHO). *Global Health Risks: Mortality and Burden of Disease Attributable to Selected Major Risks*; WHO: Geneva, Switzerland, 2009.
13. Malagoli, M.; Schiavon, M.; Dall'Acqua, S.; Pilon-Smits, E.A.H. Effects of selenium biofortification on crop nutritional quality. *Front. Plant Sci.* **2015**, *6*, 280. [[CrossRef](#)] [[PubMed](#)]
14. Wu, Z.L.; Bañuelos, G.S.; Lin, Z.Q.; Liu, Y.; Yuan, L.X.; Yin, X.B.; Li, M. Biofortification and phytoremediation of selenium in China. *Front. Plant Sci.* **2015**, *6*, 136. [[CrossRef](#)] [[PubMed](#)]
15. Shreenath, A.P.; Ameer, M.A.; Dooley, J. *Selenium Deficiency*; StatPearls Publishing: Treasure Island, FL, USA, 2020.
16. Yamada, H.; Kamada, A.; Usuki, M.; Yanai, J. Total selenium content of agricultural soils in Japan. *Soil Sci. Plant Nutr.* **2009**, *55*, 616–622. [[CrossRef](#)]
17. Wan, J.; Zhang, M.; Adhikari, B. Advances in selenium-enriched foods: From the farm to the fork. *Trends Food Sci. Technol.* **2018**, *76*, 1–5. [[CrossRef](#)]
18. Trolove, S.; Tan, Y.; Morrison, S.; Feng, L.; Eason, J. Development of a method for producing selenium-enriched radish sprouts. *LWT* **2018**, *95*, 187–192. [[CrossRef](#)]
19. Longchamp, M.; Castrec-Rouelle, M.; Biron, P.; Bariac, T. Variations in the accumulation, localization and rate of metabolization of selenium in mature *Zea mays* plants supplied with selenite or selenate. *Food Chem.* **2015**, *182*, 128–135. [[CrossRef](#)]
20. Gupta, M.; Gupta, S. An Overview of Selenium Uptake, Metabolism, and Toxicity in Plants. *Front Plant Sci.* **2017**, *7*, 2074. [[CrossRef](#)]
21. Bratakos, M.S.; Ioannou, P.V. The regional distribution of selenium in Greek cereals. *Sci. Total Environ.* **1989**, *84*, 237–247. [[CrossRef](#)]
22. Bouyoucos, G.J. A recalibration of the hydrometer method for making mechanical analysis of soils. *Agron. J.* **1951**, *43*, 434–438. [[CrossRef](#)]
23. Page, A.L. (Ed.) *Methods of Soil Analysis, Part 2*, 2nd ed.; American Society of Agronomy: Madison, WI, USA, 1982.
24. NF ISO 10693. *Détermination de la Teneur en Carbonate—Méthode Volumétrique*; Qualité des Sols AFNOR: Paris, France, 1995; pp. 177–186.
25. Loeppert, R.H.; Suarez, D.L. Carbonate and gypsum. In *Methods of Soil Analysis, Part 3, Chemical Methods*; Bigham, J.M., Bartels, J.M., Eds.; ASA-SSSA: Madison, WI, USA, 1982; pp. 437–474.
26. Olsen, S.R.; Cole, C.V.; Watanabe, F.S.; Dean, L.A. *Estimation of Available Phosphorus in Soils by Extraction with Sodium Bicarbonate*; US Department of Agriculture: Washington, DC, USA, 1954; Volume 939, pp. 1–19.

27. Nelson, D.W.; Sommers, L.E. Total carbon, organic carbon and organic matter. In *Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties*; Page, A.L., Miller, R.H., Keeney, D.R., Eds.; ASA-SSSA: Madison, WI, USA, 1982.
28. Schwertmann, U.; Taylor, R.M. Iron oxides. In *Minerals in Soil Environments*, 2nd ed.; Dixon, J.B., Weed, S.B., Eds.; 1989; pp. 379–438. Available online: http://www.scielo.br/scielo.php?script=sci_nlinks&ref=000101&pid=S0103-8478201300060000900024&lng=pt (accessed on 17 August 2019).
29. Mehra, O.P.; Jackson, M.L. Iron oxide removal from soils and clay by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Min.* **2013**, *7*, 317–327. [[CrossRef](#)]
30. Hagarová, I.; Žemberyová, M.; Bajčan, D. Sequential and single step extraction procedures used for fractionation of selenium in soil samples. *Chem. Pap.* **2005**, *59*, 93–98.
31. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1362–1403. [[CrossRef](#)]
32. Freundlich, H. Über die adsorption in lösungen. *Z. Phys. Chem.* **1906**, *57*, 385–470. [[CrossRef](#)]
33. Mirlean, N.; Seus-Arrache, E.R.; Vlasova, O. Selenium deficiency in subtropical littoral pampas: Environmental and dietary aspects. *Environ. Geochem. Health* **2018**, *40*, 543. [[CrossRef](#)]
34. Balistrieri, L.S.; Chao, T. Adsorption of selenium by amorphous iron oxyhydroxide and manganese dioxide. *Geochim. Cosmochim. Acta* **1990**, *54*, 739–751. [[CrossRef](#)]
35. Dhillon, K.S.; Dhillon, S.K. Adsorption-desorption reactions of selenium in some soils of india. *Geoderma* **1999**, *93*, 19–31. [[CrossRef](#)]
36. Söderlund, M.; Virkanen, J.; Holgersson, S.; Lehto, J. Sorption and speciation of selenium in boreal forest soil. *J. Environ. Radioact.* **2016**, *164*, 220–231. [[CrossRef](#)]
37. Sheppard, S.C. Robust Prediction of Kd from Soil Properties for Environmental Assessment. *Hum. Ecol. Risk Assess. Int. J.* **2011**, *17*, 263–279. [[CrossRef](#)]
38. Zhu, L.; Zhang, L.; Li, J.; Zhang, D.; Chen, L.; Sheng, D.; Yang, S.; Xiao, C.; Wang, J.; Chai, Z.; et al. Selenium sequestration in a cationic layered rare earth hydroxide: A combined batch experiments and EXAFS investigation. *Environ. Sci. Technol.* **2017**, *51*, 8606–8615. [[CrossRef](#)]
39. Ligowe, I.; Phiri, F.; Ander, E.; Bailey, E.; Chilimba, A.; Gashu, D.; Joy, E.; Lark, R.; Kabambe, V.; Kalimbara, A.; et al. Selenium deficiency risks in sub-Saharan African food systems and their geospatial linkages. *Proc. Nutr. Soc.* **2020**, 1–11. [[CrossRef](#)] [[PubMed](#)]
40. Nakamaru, Y.; Altansuvd, J. Speciation and bioavailability of selenium and antimony in non-flooded and wetland soils: A review. *Chemosphere* **2014**, *111*, 366–371. [[CrossRef](#)] [[PubMed](#)]
41. Rovira, M.; Giménez, J.; Martínez, M.; Martínez-Lladó, X.; de Pablo, J.; Martí, V.; Duro, L. Sorption of selenium(IV) and selenium(VI) onto natural iron oxides: Goethite and hematite. *J. Hazard. Mater.* **2008**, *150*, 279–284. [[CrossRef](#)] [[PubMed](#)]
42. Coppin, F.; Chabroulet, C.; Martin-Garin, A. Selenite interactions with some particulate organic and mineral fractions isolated from a natural grassland soil. *Eur. J. Soil Sci.* **2009**, *60*, 369–376. [[CrossRef](#)]
43. Goldberg, S. Modeling Selenite Adsorption Envelopes on Oxides, Clay Minerals, and Soils using the Triple Layer Model. *Soil Sci. Soc. Am. J.* **2013**, *77*, 64–71. [[CrossRef](#)]
44. Kosmulski, M. Evaluation of Points of Zero Charge of Aluminum Oxide Reported in the Literature. *Pr. Nauk. Inst. Gor. Politech. Wroc.* **2001**, *95*, 5–14.
45. Schwertmann, U.; Taylor, R.M. Iron oxides. In *Minerals in Soil Environments*; Dixon, J.B., Weed, S.B., Eds.; Soil Science Society of America: Madison, WI, USA, 1977; pp. 145–179.
46. Miyittah, M.K.; Tsyawo, F.W.; Kumah, K.K.; Stanley, C.D.; Rechcigl, J.E. Suitability of two methods for determination of point of zero charge (PZC) of adsorbents in soils Comm. *Soil Sci. Plant Anal.* **2016**, *47*, 101–111. [[CrossRef](#)]
47. Tan, W.; Lu, S.; Liu, F.; Feng, X.; He, J.; Koopal, L. Determination of the point-of-zero charge of manganese oxides with different methods including an improved salt titration method. *Soil Sci.* **2008**, *173*, 277–286. [[CrossRef](#)]
48. Nakamaru, Y.; Tagami, K.; Uchida, S. Distribution coefficient of selenium in Japanese agricultural soils. *Chemosphere* **2005**, *58*, 1347–1354. [[CrossRef](#)]
49. Premarathna, H.; McLaughlin, M.; Kirby, J.; Hettiarachchi, G.; Beak, D.; Stacey, S.; Chittleborough, D. Potential Availability of Fertilizer Selenium in Field Capacity and Submerged Soils. *Soil Sci. Soc. Am. J.* **2010**, *74*, 1589–1596. [[CrossRef](#)]

50. Liang, D.; Li, Z. Response to the comment by Sabine Goldberg on: Selenite adsorption and desorption in main Chinese soils with their characteristics and physicochemical properties. *J. Soils Sediments* 2015, 15, 1150–1158, doi:10.1007/s11368-015-1085-7. *J. Soils Sediments* **2016**, 16, 325. [[CrossRef](#)]
51. Antoniadis, V.; Levizou, E.; Shaheen, S.; Ok, Y.; Sebastian, A.; Baum, C. Trace elements in the soil-plant interface: Phytoavailability, translocation, and phytoremediation—A review. *Earth-Sci. Rev.* **2017**, 171, 621–645. [[CrossRef](#)]
52. Loffredo, N.; Mounier, S.; Thiry, Y.; Coppin, F. Sorption of selenate on soils and pure phases: Kinetic parameters and stabilisation. *J. Environ. Radioact.* **2011**, 102, 843–851. [[CrossRef](#)] [[PubMed](#)]
53. Garcia-Sanchez, L.; Loffredo, N.; Mounier, S.; Martin-Garin, A.; Coppin, F. Kinetics of selenate sorption in soil as influenced by biotic and abiotic conditions: A stirred flow-through reactor study. *J. Environ. Radioact.* **2014**, 138, 38–49. [[CrossRef](#)] [[PubMed](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).