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Selenium Bio-accumulation and Bio-concentration Factors in some Plant Species in an Arid Area in Central Part of Iran

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Background: Concentrations of Se in seven plant species (white mulberry, apricot, spindle tree, pistachio, wheat, barley, chives), and the associated soil samples were investigated in Shahrood and Damghan, Iran.
Materials and Methods: Soil samples were taken from the surface zone (0-5 cm) and plough zone (5-20 cm) in 13 sampling locations. The collected soil and plant samples were taken to the laboratory, then digested usin USEPA's method and analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy technique.
Results: Since there was a significant correlation (r=0.688, p<0.01) between Se concentration in the two soil's depths, it was turned out that agricultural practices, through tillage and plough, had probably moved Se to the deeper parts of the soil in area in which agricultural activity was prevalent. The highest accumulation of Se was recorded in the chives with the average value of 0.35mg kg^{-1}. Except for apricot, the concentrations of Se in top parts of the plants (e.g. leaf, grain, fruit) were higher than stem/stalk, implying the easy translocation of this element in the considered plant species.
Conclusions: The highest values of bio-concentration factors were recorded in chives followed by spindle tree and wheat, whereas the lowest level was detected in pistachio.

Keywords: *Agricultural Activity, Bio-concentration Factor, Soil pollution*

1. Background

Due to unsustainable development in recent decades, environmental contamination has become a common phenomenon, requiring continuous monitoring of different environmental matrices (e.g. soil, sediment, water, air)for various contaminants in different parts of Iran (1, 2, 3). Among the investigated elements, Se is an element which has not been considered comprehensively in Iranian ecosystems. Se has been reported to be harmful in higher than normal levels; for instance, some toxic symptoms have been detected in human at levels as high as 0.4 mg per day (4). Therefore, the bio-accumulation of this element has received attention in recent years (5). Besides natural sources of Se, mainly through geological formations, it is also introduced through anthropogenic sources, mainly via oil refinery and mining activities (6). The chemical behavior of Se is similar to that of sulfur and there are four oxidation states for Se in the environment which are selenide (-2), elemental Se (0), thioselenate (+2), selenite (+4) and selenate (+6) (7). In aerobic and neutral to alkaline environments, selenate is the dominant species whereas, in anaerobic environments selenide and elemental Se are the prevalent forms (8). As a whole, organic forms of Se are more plant available than inorganic forms. However, among different forms, selenate is more easily translocated in plant species and, therefore, more likely to be transported to above-ground parts than selenite or organic forms (9). Due to the low concentration of Se in atmospheric deposition, soil seems to be the main contributing factor for Se in plants (10). Therefore, it seems as if the bioavailability of Se in soil is the main contributing factor to the accumulation of Se in plants, but there are some contradicting results among researchers in this field. For instance, De Temmerman *et al*. (10) found that atmospheric deposition was a direct source of Se to crops. In addition, because of the easier translocation of selenate, its accumulation in plant leaves is much higher than that of selenite and organic form of Se (8). Regarding the accumulation capabilities of different plants, garlic and other *Allium* species are known to have a great potential for bioaccumulation of Se (10, 11). In this field, values of Se as high as 7 mg kg^{-1} were detected in garlic grown on Se-rich soils (11).

It has been shown that there are some similarities between bioaccumulation and translocation of sulfur and Se due to the fact that they have similar chemical properties. For example,Se can substitute sulfur in an iron–sulfur proteins (6, 12). Therefore, to assess this hypothesis, sulfur was also analyzed next to Se in soil and plant samples of this study.

2. Objective

The main objectives of this study were (i) to consider the accumulation of Se in the plant and the associated soil groups in an arid area, (ii) to study the soil-to-plant transfer factor of Se in the plant species, (iii) to investigate the possible impacts of agricultural practices on the fate of Se in the soil.

3. Materials and Methods

3.1. Study area

The study area is located in an arid environment in Kavir Namak Drainage Basin of Semnan Province (Figure 1). At the moment, there are many mining activities prevalent in the area (13). The main sources of soil and groundwater pollution have been reported to be the geological formations and mining activities in earlier research (14, 15). Because of various sources of pollution, soil in the study area is mostly contaminated with heavy metals leading to their subsequent transfer to plants (16). The water requirement is provided from groundwater resources (17), most of which is used for irrigation (18). The amount of precipitation in the region had been below the long-term annual average of 152 mm (19). This situation along with severe droughts in the past have probably resulted in groundwater quality deterioration, which has also been proved in earlier studies (17). Regarding the industrial activities in the region, there are just two industrial complexes in the area including Shahrood and Damghan industrial complexes located next to these cities.

3.2. Field and laboratory study

Seven plant species among the main cultivated plants in the study area were collected from 97 different locations, including white mulberry (*Morusalba*), apricot (*Prunusarmeniaca*), spindle (*Euonymus europaeus*), pistachio (*Pistacia vera*), wheat (*Triticum monococcum*), barley (*Hordeum vulgare*), chives (*Allium ampeloprasum* spp. *persicum*). The soil samples from the surface

(0-5cm) were also taken from the same locations that the plants were collected. In addition, to study the possible impacts of agricultural practices, such as tillage and plough, on Se levels, soil samples were also taken from two depths (e.g. 0-5 cm and 5-20cm) in thirteenlocations in the agricultural fields. In the laboratory, plant samples were thoroughly rinsed first with tap water and then with deionized water to remove dust and soil particles. Soil samples were air-dried and sieved through a 2-mm stainless steel mesh to remove stones and plant roots. Following the digestion of soil samples with nitric and hydrochloric acids in a ratio of 3:1 (HNO_3: HCl) (USEPA, 1996), the total level of Se was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) (20). Dried plant samples were ground using a stainless steel grinder (<0.25 mm) and the total content of the Se and S were detected by ICP-OES. The detection limits of Se in the soil and plant samples were 0.1 and 0.05 mg kg^{-1} and that of S was 50 mg kg^{-1} for both plant and soil samples, respectively. The potential Se accumulation by plants was evaluated by bio-concentration or bio-accumulation factor. The bio-concentration factor is the ratio of the plant tissue trace element concentration to the trace metal concentration in soil ($BCF=C_{plant}/C_{soil}$) (21).

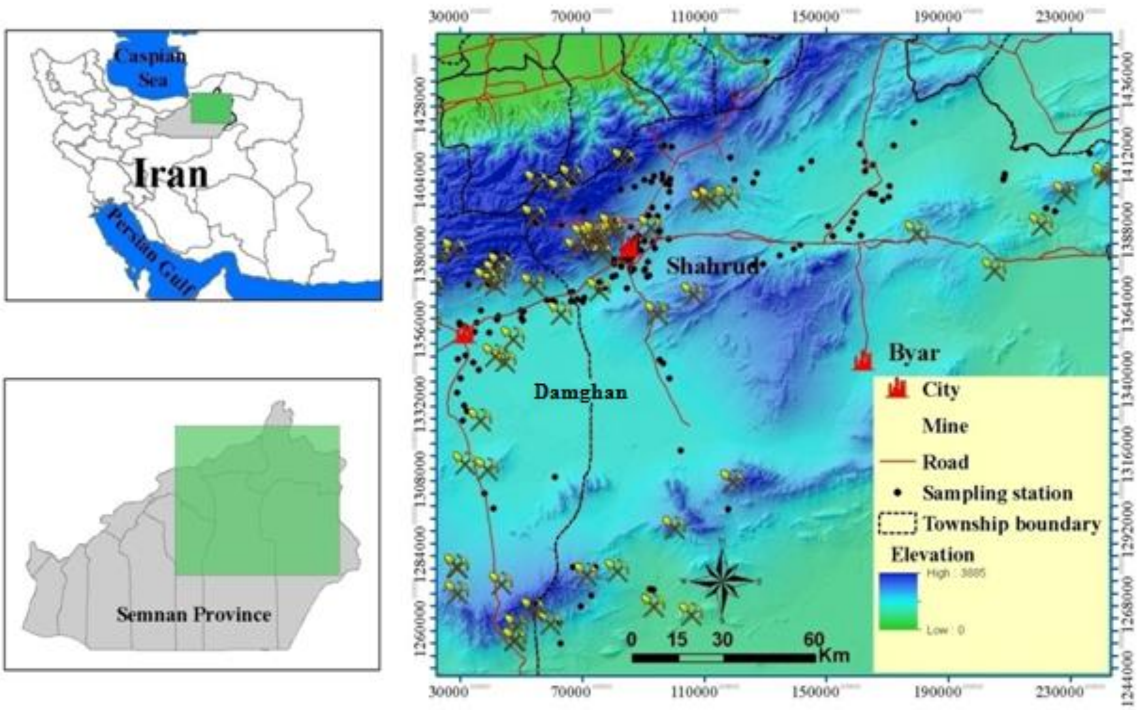

Figure1 An illustrative map of the study area in Semnan Province.

3.3. Statistical analysis

The normality of data was tested through Shapiro-Wilk test and the data transformation was implemented for those data that did not fulfill the normality requirement. To study the role of soil on the accumulation of Se in the plants, comparison between Se levels in different plant species and the associated soil samples was implemented by an analysis of variance (ANOVA) test. A paired sample t-test along with Spearman correlation was applied to consider the possible impacts of tillage on the Se values in the surface soils (0-5cm) and plough zone (5-20cm) (10) in 13 agricultural soil samples in the study area. The Spearman correlation coefficient was applied between the concentrations of Se and S in the considered plant species. In addition, Mann-Whitney U test was applied to test the significance of variation between different plant's parts for each plant species. All of the statistical methods in this study were done with SPSS v17.

4. Results

The results of analysis of variance for Se in different soil samples associated with each plant species, viz. (1) white mulberry, (2) apricot, (3) chives, (4) spindle tree, (5) wheat, (6) barley, and (7) pistachio indicated no significant difference among the soil groups (Figure 2). The mean values of Se in soil samples varied from 0.17 to 0.43mgkg^{-1}. There was a highly significant correlation coefficient($r=0.688$, $p<0.01$) between Se concentration in the two soil depths (0-5cm and 5-25cm). The ANOVA test showed significant differences among various plant species (Figure 3). Moreover, the variations of sulfur in the plant species have been illustrated in Figure 4.

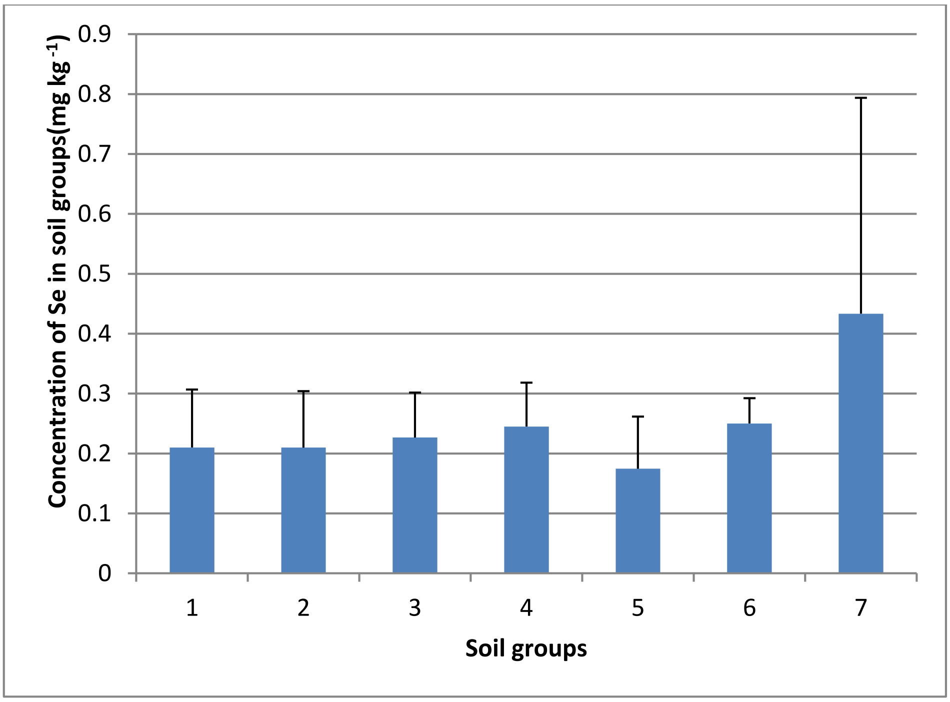

Figure 2 Mean concentration of Se in the soil groups associated with each plant species

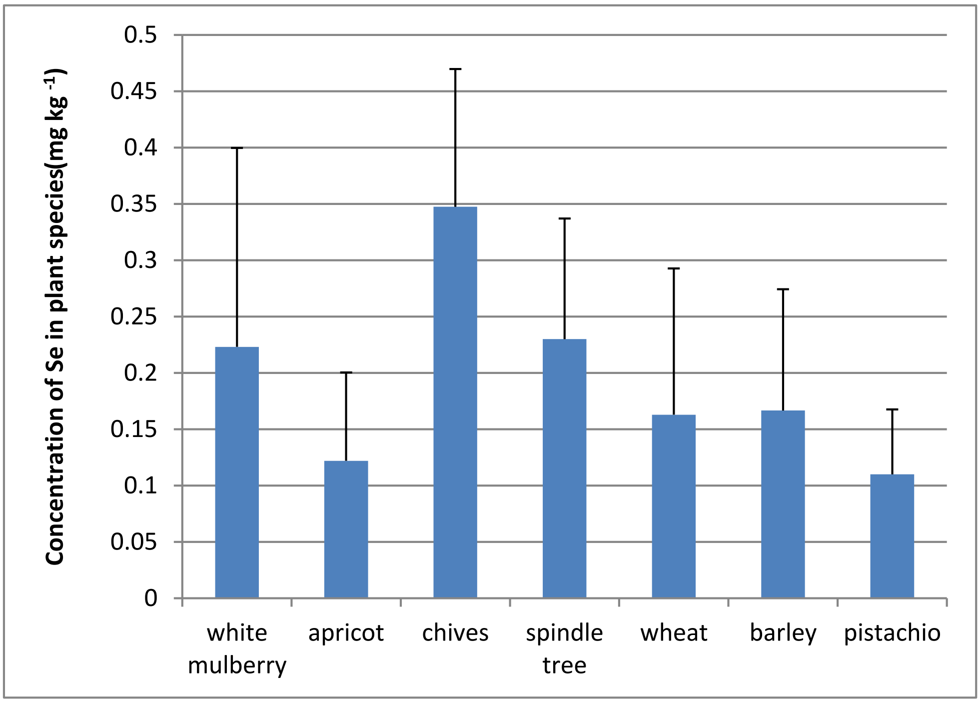

Figure 3 The mean and standard error of Se in the different plant species; significant levels are shown with different letters

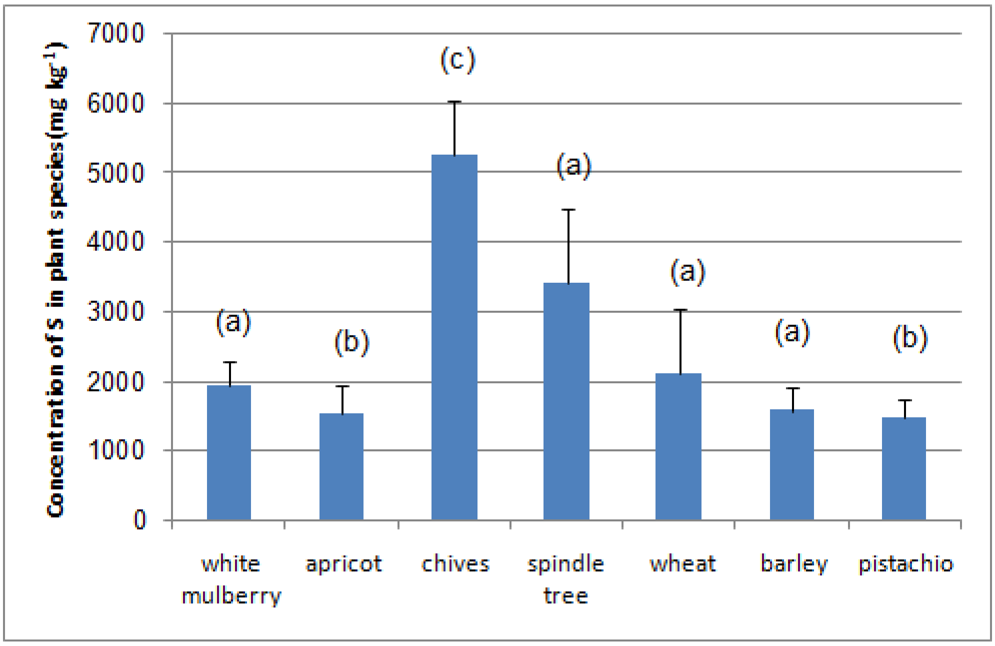

Figure 4 Mean concentration of sulfur in the plant species

The mean concentration of Se in chive (0.35 mg kg^{-1}) was significantly higher than that of other plant species. In addition, there was a significant difference between Se levels in pistachio (mean=0.11) and apricot (mean=0.12) compared with other plant types. Meanwhile, the average values of Se in different parts of plant species have been shown in Table 1.

No significant correlation between the plant's levels of S and Se was found. Moreover, no statistically significant correlation was found between the soil and plant contents of Se. On the other hand, the soil-to-plant transfer factors for Se in the plant species have been given in Figure 5.

Table 1 **The variation among Se in different parts of the plant species (mg kg^{-1})**

Plant species	Number of Samples	Standard error	Plant tissue: stem/stalk	leaf	fruit	grain
white mulberry (*M. alba*)	13	0.05		0.19	0.27	
Apricot (*P. armeniaca*)	15	0.02	0.20	0.11		
Chives (*A.ampeloprasum* spp. *persicum*)	4	0.06	0.40			
Spindle tree (*E. europaeus*)	9	0.03		0.25		
wheat (*T. monococcum*)	21	0.03	0.19			0.21
Barley (*H. vulgare*)	12	0.03	0.17			0.20
Pistachio (*P. vera*)	19	0.01		0.11		

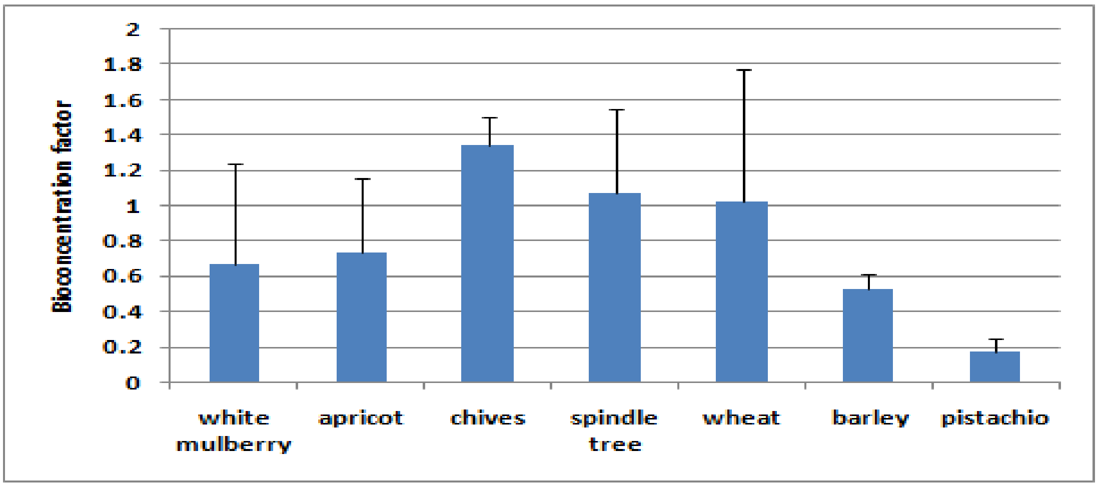

Figure 5 Bioconcentration factor of Se in the different plant species

5. Discussion

The worldwide Se concentration in soil fluctuates between 0.005 and 3.5 mgkg^{-1} with the average level of 0.33mg kg^{-1} (22). In this respect, the values detected in this study were within the worldwide range.

The study area is an arid region within Iran with an average precipitation below the long-term annual average of 152 mm (19). The soil is mainly oxidizing with high salinity and high pH levels which are common in arid and semi-arid regions (23). In oxidizing environments, selenate is the dominant form of Se, while selenite is the favored species in reducing environments (9). In alkaline well aerated soils of arid and semi-arid area, selenate (SeO_4^{2-}) is weakly adsorbed to the soil particles resulting in its higher phytoavailablity (22). Therefore, it might result in higher bioaccumulation of the total element of Se in the studied plants. Moreover, among environmental factors, temperature is the most important factor influencing Se uptake by plants, in which the rate of uptake is higher at >20°C than <15°C (9). Thus, it is expected that the rate of Se accumulation be higher in these climate conditions than other environments.

The mean concentrations of Se in the soils of north, south and central area of Iran were 0.156, 0.260, and 0.284 mg kg^{-1} (16), showing the value of central part was significantly higher. The highest amount was recorded in the arid area of Yazd (having the same climate condition as that of the current study area) with value of 0.45mgkg^{-1}, implying the higher level of Se in arid regions compared with that of wet climate zones. The mean values of Se in this study were lower than samples from the United Kingdom (0.1-4 mg kg^{-1}) (24), Scandinavia (0.42-0.57 mg kg^{-1}) (25) and Mediterranean area of Spain (0.06-1.51 mg kg^{-1}) (26), but roughly in the same range as that of Belgian soils (0.14-0.70 mg kg^{-1}) (10). The highly significant correlation coefficient between soil depths indicated that Se in the deeper parts of the soil (5-25cm) had most probably originated from the surface part (0-5cm). The main factor controlling the retention of Se in surface soil is organic matter content (27). Because of the fact that in this study about 73% of soil samples were taken from the agricultural fields, one of the possible hypothesizes in this regard is the transfer of Se bound to soil's organic matter to the deeper parts of the soil through ploughing (28). The role of soil organic matter on the Se availability in the surface soils for wheat, barley and oat has been discussed (29). The soil organic content has also been proved to be the main contributing factor influencing the availability of Se in the soils of China (30). That is to say, the higher the organic content of the soil, the lower the bioavailability of the Se will be and vice versa. Fernandez-Martınez and Charlet (31) emphasized the role of soil organic carbon on the maintenance of Se in surface soils of arid environments through avoiding precipitation of this species to deeper soil layers as well.

The lack of significant difference between the associated soil groups could most likely emanated from the accumulation strategy of these plants. Except for apricot, although the concentrations of Se in top parts of the plants (e.g. leaf, grain, fruit) were higher than stem/stalk, these differences were not significant (Table 1). This might be due to the low number of samples and high variations (high standard deviations relative the average value) that precluded statistically significant difference among plant parts. In the previous studies, there have been higher Se concentrations in the leaves of plants compared with other parts (e.g. root) (10).

There was nearly the same level of Se in grains of wheat and barley in this study. As a whole, through a literature review in various countries, the mean value of Se in arid regions was found to be higher than similar samples from humid climates (22). For instance, the overall mean values of Se in the vegetables and fruits from Greece, a Mediterranean humid country, were 6.5 µg kg^{-1} and 3.4 µg kg^{-1}, respectively (32), which were lower than 0.001 and 0.067 mg kg^{-1} found in the vegetables and fruits from Saudi Arabia, an example of arid country (33).

As the solubility of Se in soil is low, so is the level in plant samples from the majority of agricultural area, accordingly (9).The highest Se levels have been found in seleniferous and also in calcareous soils and soils of arid area (9). The wheat samples collected from different parts of Iran contained Se in the range of 0.34-1.44 mg kg^{-1} with the average level of 0.74 mg kg^{-1} (16), which was higher than that found in this research. In one study (10), the highest accumulation of Se among field crops was recorded in wheat, although the values were half of that found in leafy vegetables, which was in agreement with the result of the current study. On the other hand, pistachio was the richest source of Se among the nuts, due to the higher protein level (34). The values of Se in pistachio fluctuated between 0.32 and 0.46 $mgkg^{-1}$ with the average value of 0.40 mg kg^{-1} in the study of Nazemi *et al.* (16).With respect to different plant species, the highest value of Se in the present study was found in chive. Despite the fact that most of the fresh vegetables have low levels of Se (35), garlic, chive, and onion tend to have a greater fraction of sulfur containing amino acids and their derivatives, in addition to other sulfur compounds like glycosinolates or sulfoxides (36). In this regard, a possible reason for higher levels of Se in these plants is substitution of sulfur with Se (37). In agricultural fields of the study area, black and white fertilizers are used locally and include phosphate-rich and nitrate-rich types of compounds (17); for instance, in some areas the application rate of fertilizers have been over twofold and threefold of the government recommended values, respectively. One of the possible consequences of phosphorus fertilizer application in agricultural soils is the substitution of phosphate with selenites attached to soil particles leading to increased Se mobility and its phytoavailability (22). In this regard, phosphorus fertilizer was found to increase Se accumulation in wheat and barley in Japan, although soil-to-plant transfer factor of Se was not affected by fertilizer application [5].Other than P-fertilizer applications, the ligand-exchangeable Se desorption from the soil, as a result of P input, was another mechanism that contributed to the accumulation of Se in plants (5).

On the contrary, there is a high similarity between chemical properties of Se and sulfur, so the uptake and absorption of these elements from soil is possibly the same as well (38). Sulfate transporter in the root plasma membrane is responsible for the uptake of selenate and sulfur in plant species, which leads to the competition between these two elements for absorption by plant's root system (8). In this study, as mentioned earlier, no significant correlation was found between the plant values of sulfur and Se. Regarding the relationship between sulfur and Se, no correlation coefficient was found between Se and sulfur values in grain samples collected from UK (39), which was consistent with the results found in the current study. Although there had been some antagonistic effects between these elements in some earlier studies (e.g. 40), similar trend for Se and sulfur in different plant species was observed (Figure 3 and Figure 4). In this respect, since no significant relationship was found between soil and plant content of Se, the influence of S from fertilizers which compete with Se for plants uptake along with atmospheric deposition might had obscured the relationships between soil and plant levels of Se. Öborn *et al.* (41) did not find any correlation between the Se levels of soil with that of wheat, which was in agreement with the findings of this study. Plant ability to take up chemical elements from growth media is evaluated by a ratio of element concentration in plants to element concentration in soils, called bio-concentration factor (BCF) (9). Plants with BCF lower than one are not suitable for phytoextraction (42). Considering the soil-to-plant transfer factors found in this research, the highest value of BCF was recorded for chive, followed by spindle tree and wheat, all being higher than one. In some earlier studies, it has been claimed that the BCF values of Se in the genus *Allium* can reach as high as 1000 (43) when they are grown in Se-rich soils. On the contrary, the lowest level (0.17) was recorded for pistachio. The BCF of corn (*Zea mays L.*) for Se in China was also less than 0.1, which was comparable with the results of this study for pistachio (44).

BCF values in soils containing native Se (uncontaminated soils) are generally below 1 (45). On the other hand, the BCF of Se ranged from 0.032 to 0.046 for barley, and 0.050 to 0.054 for wheat in the study conducted by Altansuvd *et al.* (5), which were lower than the findings of this study. There were low levels of BCF for Se (varying from<0.001 to 0.146) in another study as well (46). One of the last subjects in this study was the toxicological effects of Se regarding the concentrations found in this research. The permissible level of Se in soil, based on the recommended value by the Iranian Department of Environment is 6 mg kg^{-1}, indicating that the values detected in this study were far lower than the standard levels. There is no recommended value for the total Se concentration in plant species, so no conclusion can be drawn from our results.

6. Conclusion

Se biofortification (e.g. mineral fertilization or plant breeding) is usually implemented in some countries to increase Se concentrations in edible crops. Plants with high capability for Se accumulation can be used as mineral supplements in area with deficiency of Se. In this study, three plant species, including chive, followed by spindle tree and wheat were proved to have a high potential for bioaccumulation of Se. The oxidizing environment of the soil and high temperature of arid environment are some of the possible contributing factors for the high accumulation of Se in the plant species. No significant correlation between the plant's levels of Se and S was found in this study. However, a significant correlation was observed between the levels of Se in surface and plough layers of soil in agricultural fields. In this regard, the binding of Se with soil's organic matter and its transfer to the deeper parts of the soil through ploughing is a possible explanation for this phenomenon.

Conflict of Interest

The Authors state that there is no conflict of interest.

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Authors' Contributions

Both of the authors have contributed in writing of this paper.

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تجمع زیستی و فاکتورهای غلظت زیستی سلنیم در برخی از گونه های گیاهی در یک منطقه خشک در بخش مرکزی ایران

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مقدمه: غلظت‌های سلنیم مربوط به ۹۷ نمونه گیاه متعلق به ۷ گونه گیاهی مختلف (شامل توت سفید، زردآلو، شمشاد، پسته، گندم، جو، تره) و هم‌چنین در نمونه‌های خاک در شهرهای شاهرود و دامغان در ایران مورد بررسی قرار گرفتند.

مواد و روش‌ها: به‌منظور بررسی اثرات مربوط به کشت وزرع برروی حرکت سلنیم در بین عمق‌های مختلف خاک، نمونه‌های خاک از بخش سطحی (۵-۰ سانتی‌متر) و لایه شخم (۲۵-۵ سانتی‌متر)، در۱۳ نمونه در زمین‌های کشاورزی نمونه‌برداری گردید. نمونه‌های خاک، پس از انتقال به آزمایشگاه توسط روش سازمان حفاظت محیط زیست ایالات متحده استخراج و به‌وسیله دستگاه پلاسمای جفت شده القایی مورد آنالیز قرار گرفتند.

نتایج: از آنجایی که همبستگی معنی‌دار بالایی (r=۰,۶۸۸) بین غلظت سلنیم در دو عمق مختلف خاک وجود داشت، لذا می‌توان نتیجه گرفت که فعالیت‌های کشاورزی از طریق کشت و زرع و شخم باعث انتقال سلنیم به عمق خاک شده‌اند. بالاترین میزان تجمع زیستی سلنیم مربوط به تره به میزان ۰/۳۵ میلی‌گرم در کیلوگرم بود. از سوی دیگر، به استثنای زردآلود، مقادیر غلظت در اندام‌های انتهایی گیاه (شامل برگ، میوه، دانه) بالاتر از ساقه بود که نشان دهنده انتقال آسان این عنصر در گیاهان مورد بررسی است.

نتیجه‌گیری: بالاترین میزان فاکتورهای غلظت زیستی مربوط به گونه تره و دنبال آن گیاه شمشاد وگندم در حالی که کم‌ترین میزان این فاکتور در ارتباط با گیاه پسته به‌دست آمد.

کلمات کلیدی: آلودگی خاک، فاکتور غلظت زیستی، فعالیت کشاورزی