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Chapter

Distribution of Selenium in Soils and Human Health

Muhammad Imran, Zhikun Chen, Ayaz Mehmood, Shah Rukh, Wang Weixie, Waleed Asghar and Farhan Iftikhar

Abstract

Selenium (Se) is essential as well as a toxic element for humans and animals if it exceeds a certain limit. Soil selenium plays an important role through the food chain. Total selenium in world soils ranges from 0.125 to 0.3 mg kg⁻¹ and varies with the soils' nature. High and low selenium in soils also poses serious environmental and health risks. However, in addition to selenium's overall quantity in soil, selenium reactivity, and bioavailability also depend on its chemical structure. The amount of available selenium in the soil varies depending on its oxidation state since selenium species include selenide (Se²⁻), elemental selenium (Se⁰), selenite (SeO₃²⁻), selenate (SeO₄²⁻). The pH, soil texture, amount of organic matter, and the presence of competing ions are the four most significant soil characteristics that affect Se availability. Similarly, selenium uptake and accumulation are influenced by the crop type whether it is an accumulator or not. The selenium environmental and health risk assessment is necessary to evaluate in soils with high selenium contents and crops with higher selenium uptake. Whereas in areas where selenium deficiency is observed or vulnerable to selenium, deficiency needs to be supplemented through Se inputs. The selenium deficiency and toxicity areas should be monitored carefully from a health perspective.

Keywords: total soil selenium, selenium species, selenium transformation, selenium bioavailability, selenium risk assessment

1. Introduction

A vital element for both humans and animals, selenium (Se) is a metalloid that lies in the middle of the metal and non-metal. Selenium plays a crucial role in the biological processes of human and animals body. Its high concentrations make it poisonous, and a lack of it can have catastrophic consequences on human and animal health [1]. Despite the fact that selenium has a wide range of important advantages, selenium insufficiency is becoming a widespread issue around the world. A health danger exists when selenium intake is excessive. Moreover, type II diabetes risk may be increased by a diet high in selenium [2]. A high selenium intake may enhance the expression of the transcription coactivator peroxisome proliferator-activated receptor-coactivator

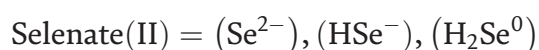
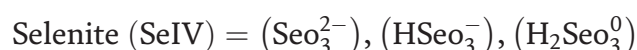
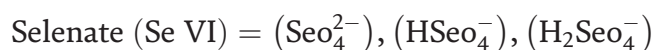
(PGC-1), which is important in cellular energy metabolism and may result in hyperglycemia [3]. Excessive selenium consumption results in loss of hair and nails, damage to the neurological system, paralysis, and even death [4]. The daily selenium consumption dosage so has significance. Selenium $40 \mu\text{g d}^{-1}$ the recommended daily allowance (RDA) suggested by the WHO [5]. An overdose occurs when the consumption for men is greater than $60 \mu\text{g d}^{-1}$ and for women is greater than $53 \mu\text{g d}^{-1}$ [6]. Responses varied when referring to various forms of selenium, and this is for the total amount of selenium.

Selenium availability from soil affects the food chain selenium level. Three major selenium mineral i.e. tiemannite (HgSe), clausthalite (PbSe), and naumannite ((Ag, Pb) Se) contains selenium and is present in soils [7]. The soil's total selenium depends on the type of parent materials and the soil-forming processes which redistribute selenium [8]. Overall, total selenium in world soils ranges from 0.125 to 0.3 mg kg^{-1} and varies with the soils' nature [9]. The essential level of selenium for animals ranges from 0.04 to 0.1 mg kg^{-1} , while a concentration exceeding 3.5 to 5 mg kg^{-1} in their food may cause harmful impacts [4, 10]. Human activities including fossil fuel and coal burning, metal smelting, inorganic, and organic fertilizer application, lime, manure, and solid sewage waste disposal cause Se accumulation in soils [11]. The selenium accumulation in soils poses serious threats to the agroecosystem via bioaccumulation [11, 12]. Selenium toxicity in soil and food chains depends on its forms and distribution rather than its total contents [13]. Total selenium concentration in soils derived from various sources ranges from 0.27 to 7.05 mg kg^{-1} [8].

Yet in addition to the amount of selenium in the soil as a whole, selenium reactivity and bioavailability also depend on the chemical form of the element. Several forms of selenium, including selenide, elemental selenium, selenite, selenate, and organic selenium, are found in soil, depending on its oxidation state [14]. The replenishment of selenium in soil solution is also aided by selenium that is contained in or bonded to various fractions in soils. Typically, there are five different selenium fractions: ion-exchangeable or calcium-bound selenium, oxides-bound selenium (iron and aluminum oxides), organic and humic-bound selenium, sulfide-bound selenium, and residual selenium. Thus, it's critical to keep an eye on the type and amount of selenium exposure through different foods grown under different soils.

2. Selenium species in soils

There are a variety of selenium species that can be found in soil solution.



Depending on the characteristics of the environment or the soil, several species of selenium can be found in the form of selenide (Se^{2-}), elemental selenium (Se^0), selenite (SeO_3^{2-}), selenate (SeO_4^{2-}). Selenate (SeO_4^{2-}): Under conditions in which it is thoroughly oxidized, selenate maintains its stability. Selenate is not absorbed by soil elements with the same level of strength as selenite [15, 16], and the transformation of selenate into less mobile forms of selenite or elemental Se) is a long process [17].

Selenate is the form of selenium that may be taken up by plants in the greatest quantity [18, 19]. Selenite (SeO_3^{2-}): Selenite is a can be found in settings that are only slightly oxidized. Selenous acid is a weak acid that can only be protonated in conditions where the pH values range from acidic to neutral. Microorganisms in acidic settings [20] or moderately reducing agents in neutral or alkaline environments [21] can convert selenite to elemental selenium. Selenite possesses a significant propensity for sorption, in particular by oxides of iron and aluminum [17, 18]. Whereas the adsorption of selenite (SeO_3^{2-}) depends on pH, and the concentration of competing anions such as phosphate (PO_4^{3-}) [22]. Selenide: Selenide (Se^{2-}) typically exists in reducing environments as metal selenides and hydrogen selenide (H_2Se) a poisonous gas with a bad smell. In water, it readily oxidizes to elemental Se [23]. Se-sulfides and metal selenides often have very low solubility [24]. Besides that, microbial activities also result in the production of dissolved organic selenide molecules or volatile methylated derivatives of selenium such as dimethyl diselenide [25, 26]. Elemental Selenium (Se^0): Elemental selenium (Se^0) exists in reduced conditions in the form of crystalline or amorphous. Red crystalline Se is alpha- and beta-monoclinic Se. Whereas the amorphous form is Red and glassy or black [27]. Elemental Se oxidize or reduce slowly and extremely insoluble in water. Specific microorganisms can oxidize elemental Se to selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}) [23].

3. Selenium solubility and transformation

Selenate and selenite are the major forms of Se in cultivated soils. The mole fractions of Se species were used to calculate the total soluble Se supported by eight selenate and selenite minerals, which might be present in soils. The effect of redox on total soluble Se at which these minerals can form in neutral soils. None of these minerals are expected to form in normally cultivated soils. Only manganese selenite (MnSeO_3) is sufficiently stable that it might precipitate in strongly acidic environments. Ferric selenite was included because several investigators reported that it might be formed in acid soils. Decreasing pH has a negative effect on the solubility of both minerals which also suggests that $\text{Fe}_2(\text{SeO}_3)_3$ is unstable with respect to MnSeO_3 . At pH 4, $\text{Fe}_2(\text{SeO}_3)_3$ and MnSeO_3 can maintain $10^{-1.5}$ and $10^{-6.7}$ M of Se in the solution. The previous studies' reported for soluble Se in acid soils appeared to be close to the solubility of MnSeO_3 . Drastic changes in pH have strong effects on precipitation/dissolution and adsorption/desorption processes in soils, and disturbed soil systems may need much longer time than pure systems to re-attain equilibrium. The concept that Se in soils is governed by an adsorption type of mechanism rather than by precipitation/dissolution reactions is accepted by most soil scientists. The sorption of Se in acid soils was related to sesquioxides.

The majority of the Se in agricultural soils exists as selenate or selenite. The sum of soluble Se can be calculated through the Se supplied through selenate and selenite minerals that could be calculated in soils by using the mole fractions of Se species. Changes in the amount of total soluble Se that are necessary for mineralization in neutral soils as a result of redox conditions. In typical agricultural soils, none of these minerals would be expected to occur. However, only manganese selenite (MnSeO_3) is stable enough to possibly precipitate in highly acidic conditions. Many researchers suggested that ferric selenite could be generated in acid soils, so it was included. Both minerals become less soluble as pH decreases, which is more evidence that $\text{Fe}_2(\text{SeO}_3)_3$

is more unstable than MnSeO_3 in acidic conditions. The compounds $\text{Fe}_2(\text{SeO}_3)_3$ and MnSeO_3 supply 101.5 and 106.7 M of Se, respectively, in soil solution at 4 pH. It appeared that the solubility of MnSeO_3 in acid soils was close to that reported in prior investigations. It may take significantly longer for disturbed soil systems to re-attain than pure systems, as large shifts in pH have profound effects on precipitation/dissolution and adsorption/desorption processes in soils. Most soil scientists agree that Se in soils is controlled by an adsorption mechanism rather than precipitation/dissolution events and sesquioxides are considered to play a significant role in the sorption of Se in acid soils.

Soil selenium can be found in a variety of oxidation states, including 2, 4, and 6. The chemical speciation and environmental stability of selenium compounds are largely controlled by redox potential and pH. The selenate species predominates throughout a wide pH range at high redox. At the middle of the redox scale, biselenite or selenite dominates depending on the pH. We anticipate the presence of elemental Se and selenide species only at low redox. The amount of Se in the liquid phase of acid soils may be regulated by adsorption and desorption processes. The chemical forms of an element in soil are regulated by the redox potential (Eh) and pH. It has been shown **Figure 1** [28] that when elemental Se is given to soils, some of it is rapidly oxidized to selenite, and that the rate of transfer from selenite to selenate and selenate to elemental Se is considerably slower. There was no correlation between soil pH and the rate of oxidation of elemental Se, but this oxidation rate did vary. In alkaline soils, selenite can be easily oxidized to selenate, while in acid soils, this process can be somewhat challenging [16]. Of all the Se oxides, selenium dioxide has the highest degree of

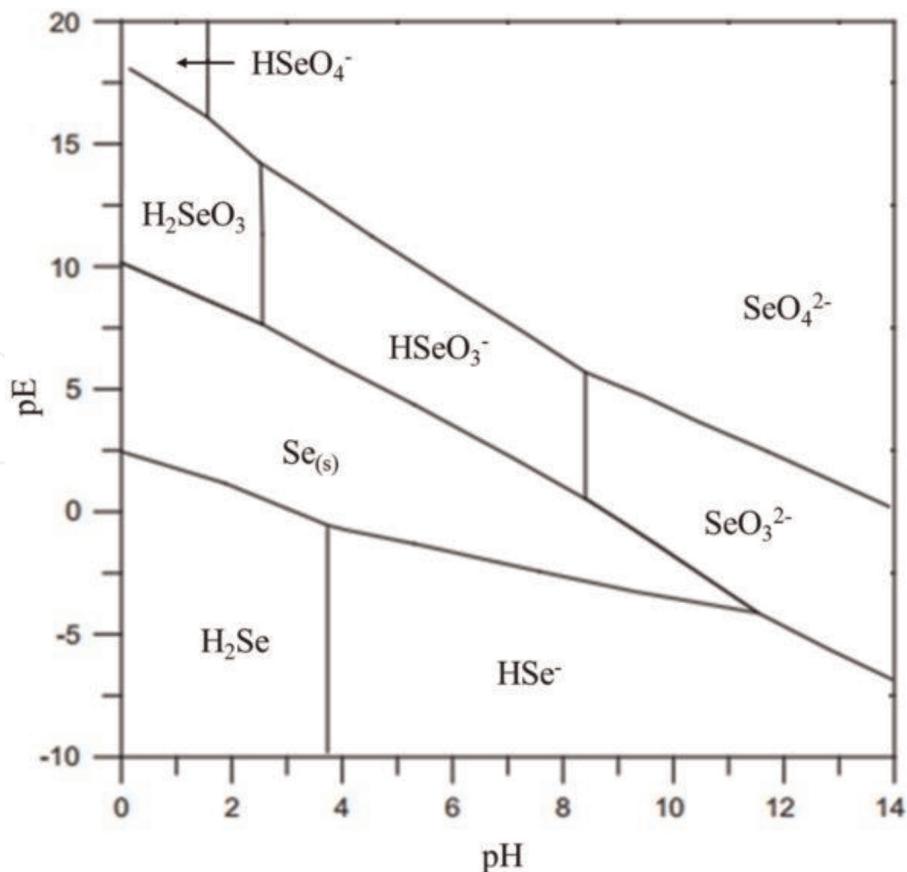


Figure 1. Selenium forms at different pE-pH levels (adopted from Seby et al. 2001).

stability. Selenium dioxide is readily reduced to elemental Se by mild reducing agents [29]. Easily dissolving in water, selenium dioxide reacts with hydrogen peroxide to produce a weak acid called selenious acid. With the help of mild reducing agents like sulfur dioxide, selenite can be quickly converted to elemental Se in acidic circumstances [25]. In dry, alkaline conditions, elemental Se persists in the form of sandstones. It has been claimed that some soils contain elemental Se because they contain bacteria and fungi that can break down selenite and selenate into elemental Se. In addition, bacteria are capable of converting elemental Se into selenite or selenate under the right conditions.

4. Selenium bioavailability

The subject of selenium (Se) uptake by plants always remained an important aspect to study, because of its direct relation to human and animal health through the food chain. The high Se concentrations in food cause adverse health effects for humans [10]. While Se plays a crucial part in a variety of biological processes, which makes it a necessary trace element for both humans and other animals. Se insufficiency has been associated with multiple ailments, both in humans and in livestock. Due to the fact that Se is both an important nutrient and an element that can be poisonous, a substantial amount of study has been done to both enhance and decrease the amount of Se that is present in plants.

The selenium uptake and accumulation by plants is a major concern because of its deficiency or toxicity through crops. To meet human and animal nutritional requirements it is very important to carefully consider the soil and crop factors to understand how uptake and accumulation in crop plants are influenced. In Se deficient regions how to increase Se concentrations in plant tissue and ultimately in the food chain. Whereas the Se-rich areas or seleniferous soils how can reduce the selenium uptake or accumulation in plants. Plant species also vary in Se accumulation. Unlike normal agricultural crops, which accumulate very little selenium, selenium accumulator plants can accumulate exceptionally high quantities of Se when cultivated in seleniferous soils [18, 23]. Yet the essential role of Se for plants is not known. Plants uptake selenate (Se^{6+}) many folds greater than selenite (Se^{4+}). whereas the elemental Se (Se^0) is difficult or impossible for plants to obtain. Plants' ability to absorb selenium is also impacted by the chemical and physical properties of the soil, including pH level, soil texture, amount of organic matter, and the presence of ions like PO_4^- and SO_4^- . The concentration of selenium (Se) in soils and plants that are poor in Se can be increased by applying selenium (Se) to the soil, the seed, and the plant leaves.

4.1 Influencing factors on selenium bioavailability

The presence of competitive ions, electrical conductivity (Eh), pH, soil texture, and organic matter content are the five most critical soil variables that influence the availability of selenium. *The Eh and pH*: Both soil Eh and pH play a significant role in determining the chemical form that selenium takes up in soils. Selenate (Se^{6+}) is the predominant form of selenium (Se) found in well-aerated, alkaline soils. Selenite (Se^{4+}) is the predominant form of selenium in neutral and acid soils. Due to its adsorption by clays and iron oxides, selenite is slightly less readily available than other forms of selenium. The oxidation state of selenium is affected by the pH of the soil (**Figure 1**), but the ability of clays and ferric oxide to adsorb selenium is also impacted by this

property [30]. Between pH 3 and 8, there was hardly any change in the amount of selenite (Se^{4+}) that was adsorbed by Fe_2O_3 . They came to the conclusion that the pH, and not the layer silicate structure, was the factor that governed selenite (Se^{4+}) adsorption on clay minerals. The effects of pH on the effect on the sequestration of selenium by plants was also observed. The greatest quantity of selenite (Se^{4+}) is available to plants when those plants are cultivated on soils with a pH range of acidic to neutral. As the pH of the soil rises, hydroxyl ions take the place of selenite (Se^{4+}) on the adsorption sites. This causes selenite (Se^{4+}) to be released into the solution, which results in an increase in the availability of the element to plants [10]. *Soil texture:* Because selenite (Se^{4+}) is absorbed by clays, the proportion of clay in the soil has a significant bearing on how well plants are able to take it up. Hence, plants are able to absorb twice as much Se from sandy-textured soil. *Organic matter:* Selenium is released and fixed in part by organic materials. Organometallic complexes may offer significant Se-adsorbing sites, and organic matter fixes the selenium by removing it from the soil solution. Because organic matter in soil serves as a source of selenium, plants absorb more of it than they would in inorganic soils.

5. Accumulation and ecological risk assessment

Selenium accumulation was quantified by calculating the index of Se accumulation (I_{geo}). The geo-accumulation index was first purposed by Müller [31], to investigate heavy metals pollution compared with their background concentration in respective soils [32], it can be defined as follows:

$$Geo - accumulationIndex (I_{geo}) = \log_2 \left(\frac{C_{Soil}^{Se}}{k \times C_b^{Se}} \right) \tag{1}$$

In the above equation, C_{Soil}^{Se} denotes the selenium contents in soils and C_b^{Se} denotes the background concentration of selenium in respective soils. Whereas, in background concentration, the k is constant and its value is 1.5. The quantification of selenium contamination in soils was classified by geo-accumulation index criteria (**Table 1**).

The selenium pollution load index (PLI) was calculated as

Geo-accumulation index		Pollution load index		Ecological risk index	
Igeo	Level	PLI	Level	ER	Level
$I_{geo} < 0$	Uncontaminated	$PLI \leq 1$	Low level of pollution	$ER < 40$	Low potential ecological risk
$0 < I_{geo} \leq 1$	Uncontaminated to moderately contaminated	$1 < PLI \leq 2$	Moderate level of pollution	$40 \leq ER < 80$	Moderate potential ecological risk
$1 < I_{geo} \leq 2$	Moderately contaminated	$2 < PLI \leq 5$	High level of pollution	$80 \leq ER < 160$	Considerable potential ecological risk
$2 < I_{geo} \leq 3$	Moderately to heavily contaminated	$PLI > 5$	Extremely high level of pollution	$160 \leq ER < 320$	High potential ecological risk

Geo-accumulation index		Pollution load index		Ecological risk index	
Igeo	Level	PLI	Level	ER	Level
3 < Igeo ≤ 4	Heavily contaminated			ER ≥ 320	Very high potential ecological risk
4 < Igeo ≤ 5	Heavily to extremely contaminated				
Igeo > 5	Extremely contaminated				

Table 1.
 Classification criteria for different indices.

$$Pollution\ Load\ Index = \left(\frac{C_{Soil}}{C_b} \right) \quad (2)$$

where C_{Soil}^{Se} is the concentration of selenium in any sample x, and C_b^i is the background concentration of selenium in soils before accumulation which was calculated for each soil by determining the Se concentration in the deepest horizon. The criteria for classifying the pollution load index is presented in **Table 1**.

The potential ecological risk of selenium accumulation to the ecosystem was calculated by the ecological risk index, which was first suggested by Hakanson [33]. The potential ecological risk index was by the following equation:

$$E_r^i = T_r^i \times \left(\frac{C_{Soil}^{Se}}{C_b^{Se}} \right) \quad (3)$$

where T_r^i is the toxic effect of selenium (Se = 10), C_{Soil}^{Se} the concentration of selenium in soil samples, C_b^{Se} is the background concentration of selenium in soils. Classifying criteria is presented in **Table 1**.

6. Health risk assessment

The USEPA approach, which has been extensively used around the world, can be used to assess the health risks associated with heavy metal exposure through food consumption [34]. By calculating the target hazard quotient (THQ) and the hazard index (HI) for selenium, the health risks of ingesting Se will be measured. Below are the equations as follow:

$$THQ = \frac{EF * ED * C_{veg} * IR_{veg}}{BW * AT * RfD} \quad (4)$$

The recommended daily intake (RfD) is the amount of selenium consumed each day through plant-based foods that are deemed to be safe over the course of a lifetime. Depending on the age, sex, and standard tolerable daily intake of Se, the range is 0.02 to 0.075 mg kg⁻¹ day⁻¹ [35]. EF stands for exposure frequency (365 days per year), ED for exposure duration (74.68 years), C for food's selenium content, IR for food's

ingestion rate, BW for average body weight, and AT for an average duration of non-carcinogen exposure (365 days divided by 74.68 years).

The following equation was used to calculate the hazard index (HI) of consuming food while simultaneously absorbing multiple heavy metals:

$$HI = \sum_i^n THQ_i \quad (5)$$

A negative effect is anticipated to be seen by the exposed population when the HQ/HI values are equal to or higher than 1 [36].

7. Conclusion

Selenium essentiality and toxicity and the narrow range between them made it very critical to keep an eye on selenium deficiency and toxicity through the food chain in humans and animals. While most of the selenium in our food is supplied through soils in our food. Whereas in soils selenium contents depend on soil parent material inheriting different selenium contents through different minerals in the soils. Besides the total selenium contents in soils, other factors also play important role in its availability to plants including, pH, Eh, clay, organic matter, selenium fractions, species, and competing ions which ultimately play a role in its deficiency and toxicity. It is necessary to monitor the food grown in different soils for selenium deficiency or toxicity. While evaluating the degree of toxicity it is necessary to calculate the selenium environmental or ecological risks and health risks associated with high selenium. In the end, it is necessary to consider the soil properties and other factors which influence selenium availability.

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Conflict of interest

The authors declare no conflict of interest.

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