Advances in Studies on Interaction between Selenium and Heavy Metal Cadmium

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Abstract Selenium is an essential functional element of the human body, and the issue of selenium accompanying heavy metals is receiving much concern. This paper expounded the form of existence of selenium and cadmium in soil and influencing factors of their bioavailability, and further elaborated the interaction between selenium and cadmium. On the basis, it provided references for further studies on the interaction between selenium and cadmium, and provided basis for establishing selenium-enriched barrier technology for crops.

Key words Selenium, Cadmium, Interaction

1 Introduction

Selenium, as an essential trace element of human body, has many biological functions and is reputed as "cancer killer" [1]. Cadmium is heavy metal element in nature and is not essential for plant and human body [2]. As one of the five toxic elements, Cadmium has high chemical activity and long-term toxicity [1-2]. Cadmium in farmland soil not only inhibits the growth of plants, but also harms human health when accumulating to certain dosage [3-4]. Some researches indicate that there is certain association relationship between soil selenium and heavy metals. This generates certain heavy metal threat to developing selenium-enriched areas, and the issue of interaction between selenium and heavy metals is receiving much concern in recent years [5-6]. However, many studies also indicate that the selenium in the environment can effectively reduce the content and availability of heavy metals in plant body [7-11]. Therefore, it is of great practical significance to study the interaction between soil selenium and heavy metal cadmium, so as to ensure the safe production of selenium-enriched agricultural products.

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2 Form of distribution of selenium and cadmium in soil and influencing factors of their conversion

Selenium is a rare dispersed element, and its distribution is uneven in nature [12]. In the world, the majority of soil contains 0.01 -2.0 mg/kg selenium and the average content of selenium is 0.4 mg/kg [13]. China is situated in the low-selenium zone, about 72% of the land has varying degrees of lack of selenium [11]. Cadmium is a common trace metallic element in nature, and it is often accompanied with zinc, copper, manganese, lead, selenium minerals. The cadmium content in majority soil of the world is 0.01 - 2.0 ppm[14]. In China, the natural soil cadmium is 0.01 -1.8 mg/kg, the average is 0.163 mg/kg. However, due to industrial and agricultural production activities of human beings, a large amount of cadmium-containing substances enter the atmosphere, and ecological environment including water and soil, leading to increasingly deteriorated environment. Soil parent material, mineral development and utilization, chemical fertilizer, atmospheric sedimentation, and irrigating water are main sources of soil selenium and cadmium. Soil parent material is a key factor determining the selenium content in soil [15-16], while the cadmium content in soil is mainly influenced by human factors. Plants absorb the selenium and cadmium mainly from soil, and their content, form, distribution and bioavailability in soil are decisive factors influencing accumulation of selenium in plant body. The forms of selenium [17] and cadmium in the soil can be divided by variety of methods, but generally divided into water-soluble, exchangeable, acid-soluble (carbonate and iron-manganese oxide bound), organic integration and residual form. It is generally believed that soil selenium and cadmium available for plants exist mainly in water-soluble, exchangeable and carbonate-bound forms. In these forms, selenate (hexavalent selenium) and selenite (tetravalent selenium) are main forms of selenium absorbed by plants. Hexavalent selenium is more easily absorbed by plants and also more vulnerable to leaching loss [18-19]; for cadmium, the inorganic cadmium is more effective than the organic cadmium for plants.

The existence form and availability of selenium and cadmium in the soil are influenced by physical and chemical properties such as soil pH, soil redox potential (Eh), organic matter content, mineral content, and soil microorganism. The soil pH is a key factor influencing the distribution of forms, conversion, and bioavailability of soil selenium and cadmium. Generally, with the increase in pH, the selenium absorption by soil declines. Selenium exists mainly in the form of selenate which is easily soluble in water, so the plant availability is the highest, and it is vulnerable to leaching loss [20]. In contrast, soil water-soluble and exchangeable cadmium content declines and the availability drops. In weak acid soil, selenium exists in the form of selenite. It is easily soluble in water, but strongly absorbed by soil iron oxide or ferric hydroxide, so the availability is relatively low. Under this condition, with the decline in soil pH, carbonate form cadmium is easily released into environment, the mobility and biological activity increases, while the activity of iron-manganese compound bound form and organic form cadmium declines. The influence of soil pH on cadmium form and availability is not single progressive relationship. In red soil, Liao Min *et al.* [21] found that when pH is below 6.0, the bioavailability of cadmium increases with the rise of pH; when pH is above 6.0, the bioavailability of cadmium declines with the rise of pH. In general, in certain range of pH, increasing soil pH, the availability of soil selenium increases, while the availability of cadmium declines, therefore, it is possible to control the bioavailability of selenium and cadmium in soil through adjusting soil pH. The soil redox condition directly influences forms of selenium and cadmium in soil. Under the condition of oxidation, the availability of selenium obviously increases, while the less soluble CdS in soil ix oxidized, and Cd^{2+} floats in soil solution, which deteriorates pollution. In the soil under strong waterlogging, selenide occupies the dominant position, selenide is insoluble in water and plant is difficult to absorb [22]; Cd^{2+} in soil is converted into insoluble CdS and exists in the soil, and the activity declines. Soil Eh is unstable with the change of environment, so that the biological toxicity of cadmium also changes. Thus, it is possible to reduce the available cadmium in soil through adjusting the soil redox potential. In natural conditions, the soluble selenium content is very little. However, through long-term weathering and farming, selenium can be accumulated in soil organic matters. The content of soil soluble selenium increases with the increase in soil organic matters and clay content. The soil organic matter exerts a negative effect on iron-manganese oxide bound selenium content, and exerts a positive effect on exchangeable selenium, organic selenium and residual selenium. In general, selenium combined with fulvic acid has high plant availability, while selenium combined with humic acid is difficult to be absorbed by plants. Soil organic matter plays an important role in the process of cadmium conversion apart from pH, because organic matters contain a large number of functional groups, have complexing /chelation reaction with cadmium, and the specific surface area and the adsorption capacity of cadmium iron are much higher than other mineral colloids. Similarly, soil clay has huge specific surface area and rich surface charge and superior mobility, which will accelerate the process of cadmium adsorption by soil. In addition, iron-manganese oxides in soil, especially manganese hydroxide, have strong adsorption capacity to cadmium, and will influence the cadmium migration and conversion in soil. Under the condition of strong reduction, iron-manganese oxides are reduced to ferrous manganese and form complex ferrous and complex manganese with organic matters, and the adsorbed cadmium is released, which affects the activity of cadmium. Soil microorganisms play an important role in the migration and conversion of soil selenium and cadmium. Some soil microorganisms have functions of generating volatile selenium, degrading rhizosphere organic selenium and reducing selenite generating selenium, so as to change form and concentration of soil selenium. Similar to selenium, microorganisms can reduce the bioavailability of cadmium in the soil by reducing their bioavailability, and some microorganisms can absorb heavy metals and reduce the content of heavy metals in the soil, reduce the activity and toxicity of heavy metals in the soil by the oxidation or reduction of their heavy metals [23-24]. At the same time, microorganisms can also affect plant microenvironment and reduce absorption of heavy metals [25-26]. Besides, the coexistence of ions in the soil also affects cadmium availability. Silicon and lignin are all important components of cell wall and they enhance the cell wall tightness and robustness, so cadmium ions form a natural defense mechanism when penetrating into cells. Calcium, ammonium and potassium ions also exert a certain influence on Cd availability. Calcium, zinc, and potassium ions, as competitive ions of Cd, compete for the absorption sites with Cd, while the ammonium ions influence Cd absorption mainly through changing chemical properties of soil [27]. Selenium and cadmium in the soil are greatly influenced by the soil pH and Eh, and changing soil physical and chemical properties can change the form of selenium and cadmium in the soil. When the two coexist, selenium and cadmium also have a mutual effect on each other. Shen Yanchun [6] studied the selenium-enriched areas in Guichi, and found that the three heavy metals (cadmium, mercury and arsenic) in the surface soil are associated with selenium and have certain synergistic effect. In the selenium-enriched soil, the mass fraction of cadmium is higher, and the differences of forms are great. Among them, the three forms (residual form, ion exchangeable and iron-manganese oxide bound) take up the leading position. According to some researches, the effect of selenium on soil cadmium is related to cadmium concentration. When cadmium concentration is low (0.5 mg/kg), exogenous selenium could effectively reduce cadmium content and reduce the bioavailability of cadmium; when cadmium concentration is high, the distribution of soil cadmium is stable, and such inhibition is not obvious [28-29].

3 Interaction between selenium and cadmium in plants

At present, crop variety screening, selenium fertilizer application and other biological strengthening measures have become the main ways to produce selenium-enriched agricultural products. Studies have shown that the amount of exogenous selenium can increase plant selenium content and reduce the accumulation of heavy metals in crops. As early as in 1973, Francis *et al.* [30] had found that increasing selenium concentration in plants can significantly reduce the cadmium concentration in plants. The appropriate concentration of selenium has a certain mitigation effect on cadmium poisoning. The application of selenium or foliar selenium fertilizer can alleviate the toxic effects of cadmium stress on growth of rice seedlings, inhibit the absorption of rice roots and leaves to cadmium, and reduce the cadmium content of nutritive organs, unpolished rice, and polished round-grained rice [31-33]. The antagonistic action of selenium on heavy metal cadmium is not only reflected in rice, but also reflected in other plants. When the selenium and cadmium coexist in the soil, the appropriate amount of selenium can inhibit the absorption of cadmium by turnip, strawberry, rapeseed, and potato and other crops [34-37]; when the soil cadmium and other heavy metal elements coexist, the appropriate selenium can inhibit the absorption of plants to two or more heavy metal elements. Li Zhengwen *et al.* [38] found that selenium-enriched rice varieties show the tendency of accumulation of heavy metal Cu and Cd. The field test of He *et al.* [39] also showed that application of selenite to Pb and Cd stressed *Lactuca sativa* L. significantly reduced the content of these two heavy metals in ground parts of plants. We carried out rice experiment in many areas in 2014 - 2015, and found that application of exogenous selenium can increase the accumulation of selenium in rice and reduce the cadmium content of rice grain by 40% - 70%. Many studies have found that application of exogenous selenium can effectively reduce the absorption and accumulation of heavy metal cadmium, but it should be noted that selenium is beneficial to creatures at low concentrations, but high concentration of selenium presents toxicity similar to heavy metals. Besides, when selenium concentration is too high, it does not reduce the accumulation of heavy metals, but will increase the absorption of heavy metals. Yu Suhui *et al.* [40] found that when the mass fraction of selenium in solution is lower than 250 μg/L, selenium can alleviate the toxic effect of cadmium on rice growth; when the mass fraction of selenium in solution is higher than 500 μg/L, selenium does not alleviate the cadmium stress; when the mass fraction of selenium in solution is higher than 800 μg/L, selenium and cadmium generate synergistic effect, which increases the toxic effect of cadmium on rice. Liu Yan [36] found that when the selenium concentration is lower than 15 mg/L, rape growth is promoted and the accumulation of cadmium is inhibited; when the selenium concentration is greater than 15 mg/L, the rape showed serious toxic effect of heavy metals. The antagonistic effect of selenium on heavy metal accumulation is influenced by various factors such as selenium and heavy metal concentration and form. Tie Mei *et al.* [35] found that when the concentration of selenium in the soil is lower than 1.5 mg/kg, it has antagonistic effects on cadmium content < 5 mg/kg and can promote the growth of turnip. When the selenium concentration in the soil is lower than 1.5 mg/kg, the concentration of 5 mg/kg cadmium does not affect the absorption of selenium by turnip; when the selenium concentration in soil is 5 - 10 mg/kg, the cadmium influences absorption of selenium by turnip, but the selenium in turnip is still stably accumulated; when the soil selenium concentration is higher than 10 mg/kg, the cadmium will inhibit the absorption of selenium by turnip. There has been report about mechanism of low concentration of selenium alleviating cadmium toxicity. In these processes, cadmium will exert a certain toxic effect on the plants. At present, it is generally believed that the toxic mechanism of heavy metal cadmium on plant organisms is realized mainly through following types. (i) Cadmium can occupy the calcium channel and enter the cell, leading to imbalance of steady-state calcium within cells. (ii) Through binding with enzyme type hydrosulfide group or replacement function, cadmium replaces with enzyme metals, reduces the activity of antioxidant enzyme and ability of scavenging free radicals, leading to oxidative damage. (iii) Cadmium can induce the formation of metallothionein, metallothionein participates in absorption, migration, excretion and accumulation of cadmium in plants. Selenium can reduce the accumulation of cadmium in plants, possibly because it plays a role in the above three mechanisms. Studies have found that selenium can increase the content of non-protein thiol (NPT), promote complexing of cadmium, increase the adsorption of cadmium on cell wall, so as to reduce the absorption of rice to cadmium [41]. Besides, selenium can reduce the accumulation of active oxygen, balance the nutritional elements, and increase the activity of H^{+-} and Ca^{2+}-ATP in rice [42]. Zhang Haiying *et al.* [43] also found that selenium can remove the membrane lipid peroxidation product malondialdehyde (MDA), protect the integrity of the cell membrane and reduce the content of heavy metal ions; Lu Xuanzhong *et al.* [44] pointed out that selenium, as the activity center of GSH-Px, can affect the protection system of entire enzyme through inducing activity of GSH-Px. The experiment of spraying on lettuce leave can significantly reduce the cadmium absorption. Chen Ping *et al.* [45] also found that selenium can effectively improve the enzyme activity, increase the leaf chlorophyll content, alleviate the inhibition of cadmium to growth of rice seedlings, and selenium can alleviate the damage of cadmium induced superoxide free radicals to rice. In the rapeseed leaves, cadmium treatment can degrade the chloroplast in young leaves, leading to significant decline of photosynthetic efficiency. Little selenium is favorable for keeping the stability of thylakoid and chloroplast matrix, increase the content of unsaturated fatty acids and improve the cell membrane mobility, reduce the lipid peroxidation of rapeseed seedlings, so as to alleviate the toxic effect of heavy metals on plant membrane structure and photosynthetic system. Similar experimental conclusions are also reflected in ryegrass, lettuce, potato and other plants. From the above studies, selenium can reduce the concentration of heavy metals in plants, mainly through the following four mechanisms: (i) reducing oxidative stress;

(ii) directly inhibiting the absorption of heavy metals; (iii) restoring chloroplast and increasing chlorophyll content; (iv) restoring the cell membrane quality.

4 Conclusions

There have been considerable advances in researches about the interaction between selenium and heavy metal cadmium. However, most studies focus on the effect of selenium on heavy metal cadmium, and the mechanism is mainly concentrated on antioxidant function of selenium, and most researches remain at the level of describing physiological and biochemical response. Therefore, it is necessary to study the interaction between selenium and cadmium from following aspects. (i) Heavy metals, in turn, have a very complex effect on the selenium absorption and metabolism of plants, possibly because synergistic or antagonistic effect is generated from different plant types and positions and selenium content and forms. Therefore, the relationship between the antioxidant system and the selenium, the concentration of heavy metals, and the relationship between the species are still to be explored. Besides, the effect of cadmium on the migration and conversion of selenium in crops and reduction of harm of cadmium are of great significance. (ii) There have been extensive researches about the inhibition function of calcium, zinc, potassium ions and silicon to cadmium, while there are few researches about the availability of selenium and cadmium under the condition of coexistence of selenium and cadmium. Therefore, it is recommended to strengthen the researches about the interaction between selenium and cadmium and other elements in the study of the mechanism of cadmium enrichment and cadmium barrier. (iii) On the basis of studying the mechanism of interaction between selenium and heavy metals, it is necessary to carry out a large number of field experiments to combine the selenium-enriched technology of crops with the toxic effects of heavy metals, and apply the technology into ecological agriculture to benefit human beings.

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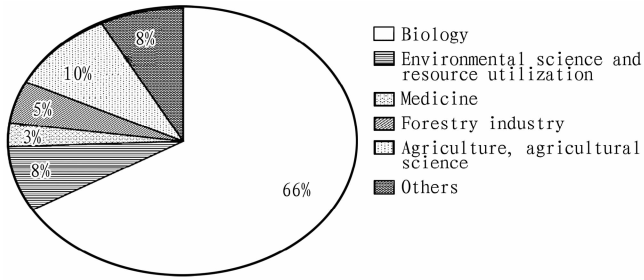

Fig. 5 Research object of bryophytes in China

4 Conclusions

The results show that the Chinese bryophyte studies mainly focus on biology, agronomy and agricultural science. The research level mainly stays in basic and applied basic research. From different research units, different journals and different authors, it is found that the regional distribution of research units is not balanced, the researchers are more scattered, and the research cycle is short. Most scholars' bryophyte studies are not very deep, the distribution of bryophyte literature is extremely unbalanced in the journals, and the researchers are particularly scattered. These problems have restricted the current bryophyte research and it is necessary to focus on other aspects and basic theoretical part. The study of bryophytes in Tibet has been the focus of attention of many experts and scholars.

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