



Botanic Metallomics of Mercury and Selenium: Current Understanding of Mercury-Selenium Antagonism in Plant with the Traditional and Advanced Technology

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Abstract

The antagonistic effect between mercury (Hg) and selenium (Se) is conclusively established in animals and human beings in the past decades. However, the underlying mechanisms of the interactions between Hg and Se in plants, as well as the metabolism of Hg–Se compounds in crops are still far from being understood. The botanic metallomics of Hg and Se mainly focuses on the translocation, transformation, and metabolism of Hg and Se in the environmental and botanic systems employing metallomics methods. An adequate understanding of the biological behavior of Hg and Se in plant is beneficial for sequestration of Hg and Se in soil–plant systems with high Hg and Se contamination. It can also provide a molecular mechanistic basis for Se supplementation in Se-deficient areas. Here, the key developments in current understanding of Hg and Se interactions in plants are reviewed. The metabolism and antagonism of Hg and Se in various plants, as well as the advanced analytical methods commonly used in this field, are summarized and discussed. As suggested, plant Hg and Se uptake, metabolism, and antagonism can be taken into account for detoxification and remediation strategies for the reduction of Hg and Se in the food chain.

Keywords Mercury · Selenium · Plant · Antagonism · Advanced analytical methods

Given the potential health threat of mercury (Hg), as well as the endorsement of Minamata Convention on Mercury in 2013 which went into effect in 2017, concern over Hg control has increased throughout the world in recent years. The toxicity of Hg, as well as migration, bioavailability, and transformation, are closely correlated with its chemical forms in the environment (Stein et al. 1996; Liu et al. 2018). As documented, DOM-Hg has the most migratory ability of various Hg species in soil while the migration of HgS is

much lower than the others (Gai et al. 2016), which in turn impacts the distribution, accumulation, and bioavailability of different Hg species. The main sources for human Hg exposure are Hg-containing food, such as fish and crops (Storelli and Marcotrigiano 2000). In south China, it was reported that human exposure to Hg was largely through rice consumption, especially in Hg-contaminated areas (Feng et al. 2007). As a sulfur analogue, Selenium (Se) is well known as an essential micronutrient for animals and human beings (Arthur and Brown 2001). It is also a beneficial nutrient for many plants including some higher plant taxa (Zhu et al. 2009), although Se being essential to plants is still a matter of controversy. Like Hg, the main source of human Se intake is via consumption of plant based foods, especially cereals (Hartikainen 2005). For most areas in China, soils are of Se-deficient although high Se concentrations have been reported in some areas, such as Enshi, Hubei Province (Yuan et al. 2012). Because of the low levels of Se in most plant foods, the average Se intake might be insufficient to meet the requirement of human health. Se supplementation on crops should be an efficient approach to improve Se content in people's daily diet. As previously reported, Carvalho et al.

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(2003) carried out inorganic and organic Se supplementation on four agricultural crops and found that low Se supplement (1.5 mg/kg Se in soil) promoted plant growth and Se accumulation in the edible parts.

Hg and Se having been continually released into the soil, sediment, and water via natural and anthropogenic pathways, chemically converted into more toxic forms and can biomagnify through the food chain. This accumulation is closely linked to environmental quality and food safety (Horvat et al. 2003). Hg and Se have specific properties making them be quite correlated with each other. Investigations into how Hg and Se interact in the environment, as well as understanding their fate through the food chain, is meaningful to protecting human health and minimizing their environmental impact. Studies of Hg and Se environmental metallomics mainly focus on the biological and systematic understanding of the translocation, transformation, metabolism, and their roles in the environment. As we know, selenols are even more reactive toward Hg than thiols, which leads to a prominent antagonistic effect between Se and Hg in organisms (Clarkson 1997). One of the earliest studies on Se–Hg antagonism was reported by Parizek and Ostadalova (1967) in laboratory rats from kidney intoxication by inorganic Hg. Subsequent studies have confirmed Hg–Se antagonism as a widespread phenomenon in microbes, aquatic organisms, birds and mammals (Dang and Wang 2011; Hoffman and Heinz et al. 1998). The total Hg and Se accumulation in these organisms have also been found to vary concurrently, commonly following an approximate 1:1 molar ratio in the specific tissues (Koeman et al. 1975). It is noteworthy that the safe range between Se essentiality and toxicity is quite narrow, thus the additive even synergistic effects of Hg and Se may occur in organisms (Palmisano et al. 1995). Many studies have confirmed Hg and Se antagonism in animals, however, the interactions between Hg and Se in plant are rarely reported although antagonism in the natural (natural soil, water, etc.) and artificial environment (cropland, crops, etc.) are very common. For example, the co-existence of high Hg and Se (tiemannite) in Wanshan District (Guizhou, China) leads to limited Hg and Se accumulation in the local plants (Zhang et al. 2012; Zhao et al. 2013b). As for the Se-deficient fields, Se supplementation does not merely increase Se content but also decrease Hg concentrations in crops. Plant food consumption, as a dominant pathway for human Hg and Se intake, is pivotal to our food safety. However, the in vivo presence and metabolic pathways of Hg and Se compounds under physiological conditions in plant are still far from being understood. The antagonistic mechanism between Hg and Se in plant also remains elusive. Herein, we summarize the state of art of Hg and Se antagonism in plant, as well as the utility of the traditional and advanced metallomics techniques commonly used in this field, including atomic fluorescence spectrometry (AFS),

inductively coupled plasma mass spectrometry (ICP-MS) and the synchrotron radiation (SR) based techniques. Our aim is to provide theoretical basis for the evaluation of food safety in areas contaminated with Hg and Se and the development of effective phytoremediation strategies to minimize the negative impact of Hg and Se.

Atomic fluorescence spectrometry (AFS) has been widely used for analysis of Hg and Se in the environmental specimens. The AFS method has advantages of high sensitivity and low detection limit (DL) ($< 0.1 \mu\text{g L}^{-1}$ for Hg and Se) (Cai 2000). For Hg quantification, the On-line total Hg and MeHg analyzers are usually applied for continuous monitoring of Hg or MeHg in the aqueous solutions. The total Hg after reduction in the liquid is blown off and brought into the optical element, then detected by UV with high sensitivity ($\text{DL} < 0.1 \mu\text{g L}^{-1}$ Hg). It has been proven to be reliable and accurate in previous works (Gu et al. 2011; Luo et al. 2017). Compared with AFS, the Hg and MeHg analyzer, although designed based on the traditional theory of atomic analysis, do not require amalgamation, have little interference and a much lower DL. Inductively coupled plasma mass spectrometry (ICP-MS) is another classical method for metallic element detection with advantages of high sensitivity and accuracy. It can also be used for instantaneous analyses of multiple elements and isotopes. For simultaneous detection of various Hg or Se species, HPLC is always hyphenated with a spectrographic or mass-specific detector for element quantification with an ideal resolution and high sensitivity (Yin et al. 2008). For plant specimens, with the application of HPLC-ICP-MS, inorganic Hg and organic Hg (mainly MeHg species) in rice root and shoot were separated and quantified in 12 min with a relatively high resolution (Xu et al. 2016). McNear Jr et al. used capillary reversed phase LC-ICP-MS (capRPLC-ICP-MS) to investigate the metabolic fate of Hg and Se in the rhizosphere of *Allium fistulosum* with advantages of element-specific and high sensitivity (McNear et al. 2012). Size exclusion chromatography (SEC)-ultraviolet (UV)-ICP-MS (SEC-UV-ICP-MS) is also an ideal method for analyses of Hg and Se containing compounds in plant. With this method, Yathavakilla and Caruso (2007) et al. analyzed Hg and Se containing compounds in soybean root. The Hg–Se complexes in soybean root were well separated with a high resolution.

The advanced nuclear analytical methods, with advantages of high sensitivity, accuracy and precision, low matrix effects, and non-destructiveness, have been playing important roles in understanding the environmental and biological activities of trace and abundant elements. For example, the neutron activation analysis (NAA), proton-induced X-ray emission technique (PIXE), isotope dilution (ID), and the synchrotron radiation (SR) technology are widely used for chemical speciation analysis of target elements in the environmental and biological samples

(Gao et al. 2007). Here, we mainly focus on the regularly applied SR based-techniques in environmental science in recent years.

SR-based techniques can give information on the content, species, localization and chemical structure of the element at a high resolution. The commonly used SR techniques in environmental science, especially for metal analyses, includes SR X-ray fluorescence (SR-XRF), SR X-ray absorption spectrometry (SR-XAS), and SR-based scanning transmission X-ray microscopy (SR-STXM). SR-XRF, belonging to an atomic method and often cataloged as a nuclear technology based on the nuclear facilities, is a multielement analytical method with a sub- $\mu\text{g g}^{-1}$ sensitivity for many metal and metalloid elements. Based on the continuous development of SR techniques in X-ray optics, the hard X-rays can be focused to submicron, even to nanometer spot size level (Gao et al. 2008), which makes it possible for imaging element distribution at cell size and giving semi-quantitative information of the target elements in the environmental and biological samples. As the size of the excited X-ray can be regulated with a slit or focusing system, the SR-XRF technique can also be applied for direct elemental determination in the specific protein bands or spots after isolated by the 1-dimensional (1-D) and 2-dimensional (2-D) electrophoresis (Gao et al. 2005). Zhao et al. (2015) detected at least 157 Se-containing protein spots using SR-XRF after the 2-DE separation of the total proteins in Se-enriched yeast. The DL of SR-XRF for Se quantification in these spots can be calculated to be $0.20 \mu\text{g g}^{-1}$. In another report, the Hg and/or Se combined proteins relating to Hg and Se antagonism in rice root were successfully identified using 1, 2-DE and SR-XRF techniques (Li et al. 2018). Apart from the relatively high resolution, another advantage of SR-XRF is in situ analysis without destroying the specimens. As a result, the tested samples can be retrieved for further amino acid identification. XAS technique, including X-ray absorption near edge structure spectrometry (XANES) and extended X-ray absorption fine structure spectrometry (EXAFS), can be employed to measure the local structure characterizations of the elements, and give information of element species, valence state, atomicity, and compound forms (Gao et al. 2007). XRF-XAS combined method can be used for in situ analyses of element localization and speciation. To date, many studies have employed XRF-XAS to investigate the distribution and speciation of Hg and Se in plant (Carrasco-Gil et al. 2013; Li et al. 2015; McNear et al. 2012).

Despite the advantages described above, as an analytical method depending on the SR photo-source, SR-XRF and SR-XAS have their own limitations, including the limited numbers of SR facility throughout the world, the long testing time, and the relatively high DL comparing with ICP-MS, AFS, and CVAAS. Therefore, the SR-XRF, SR-XAS and other SR techniques have always been used combined

with the traditional methods, even as supplementation in the complex environmental sample analyses.

Plants, being at the bottom of food chain in terrestrial systems, can accumulate high levels of Hg and Se. Investigations into how these elements interact in crops, as well as how to manage their fate, are pivotal to protect human health and minimize their environmental impact.

It has been observed that Se can protect plant from phytotoxicity by both IHg and MeHg. The accumulation and speciation of Hg in plant can be largely reduced and altered by adequate Se addition. For instance, the concentration of total Hg was reduced by Se in many plants, including radish, Indian mustard, soybean, green onion, and rice (Afton and Caruso 2009; Mounicou et al. 2006; Shanker et al. 1996; Yathavakilla and Caruso 2007; Tang et al. 2017). The distinct phytotoxicity of Hg and Se depends on their exposure doses. Shanker et al. (1996) studied the interactions of Hg and Se in Radish using a series of exposure levels of Hg and Se. They found a rapid decline of Hg concentration in the root with increasing Se and speculated the formation of HgSe complexes in the rhizosphere. Thangavel et al. (1999), in their experiment with portulaca oleracea, found that the protection of Se against Hg phytotoxicity was effective only at low (less than 0.5 ppm) concentrations. With the increase of Hg and Se concentrations, the protection decreased, and the synergistic toxicity became prominent. The ideal Hg:Se ratio for Hg and Se interaction might be close to 1:1. In a field study, Zhang et al. (2012) found there was a positive correlation between Hg and Se in the rice roots where a pattern similar to 1:1 molar ratio of Hg and Se was obviously demonstrated. In a pot experiment, Wang et al. (2016a) also reported the reduction of soil net MeHg production under proper Se amendment. The reason for Se inhibiting MeHg accumulation in rice might be attributed to the formation of MeHg–Se compounds or decrease of MeHg production in Se added paddy soil. As for different Se species, selenite and selenate play similar roles in detoxification of Hg phytotoxicity in rice (Wang et al. 2016b). To evaluate the effect of Se addition on Hg uptake by rice, in a field study, Li et al. (2015) carried out a series of Se supplementation to the paddy soils polluted with Hg. They found that Se at 0.5 mg Kg^{-1} has the highest efficiency in reducing Hg accumulation in rice and improving the rice yield. Additionally, the effective and safe Se treatment dose depends on the active Hg concentrations in soil and Se accumulation rate from soil to rice.

Generally, Hg uptake by root can be prevented by Se via the way of immobilizing Hg in the ambient or the rhizosphere. With the help of SEC-RPLC-ICP-MS, McNear et al. (2012) found that, in green onion, Hg and Se were both predominantly sequestered in the root fraction due to the formation of Hg–Se compounds, which blocked the upward translocation of Hg and Se. This phenomenon was

also found in some other plants, such as Indian Mustard (Mounicou et al. 2006). For visualizing Hg and Se in plant, SR-XRF coupled with SR-XAS is often applied to imaging the distribution and speciation of Hg and Se in different plant tissues. With the application of SR-XRF, Zhao et al. (2013a) revealed the distribution of Hg and Se in garlic root, bulb and leaf after co-exposure to Hg and Se. After locating the Hg and Se concentrated spots, species of Hg and Se were in situ analyzed using SR-XAS (Zhao et al., 2013b). The similar distribution of Hg and Se in root suggested the Hg–Se interaction, whereas the different distribution of Hg and Se in bulb implied the distinct transportation pathway of Hg and Se from root to shoot. The presence of S–Hg–S– and –HgSe– like compounds was identified in Hg and Se concentrated spots. Furthermore, Meng et al. (2014) used the SR-XRF and SR-XAS to characterize the distribution and species of Hg in rice grain and found that Hg mainly distributed in the aleurone layer in the form of Hg–cysteine and MeHg–cysteine. In another study, the antagonistic effect of Se on Hg in soil–rice system was investigated, in which the SR-XRF data showed a significant decrease of Hg in the aleurone layer and embryo part of rice grain by Se (Zhao et al., 2014). Subsequently, Wang et al. (2016a) detected HgSe containing nanoparticles in incubated paddy soil using TEM–EDX and XANES, as well as a decrease in net MeHg production. They concluded that largely reduced MeHg accumulation in rice grain was likely due to antagonistic effect of Se on Hg in soil and root. The antagonistic effect of Se on MeHg toxicity in the aqueous phase has been reported in previous studies (Jin et al., 1997; Khan and Wang 2010). Se-aided MeHg demethylation has also been demonstrated to occur in marine animals (Storelli et al. 1998) and chicken liver and kidneys (Cabanero et al. 2006). As for the mechanism, there is a hypothesis that Se in glutathione peroxidase (GP_x) can decompose the peroxides generated in the MeHg containing environment, which in turn would initiate the MeHg breakdown (Ganter 1978). A more plausible pathway of Se-induced MeHg demethylation is through the formation of bio(methylmercuric)selenide, which is unstable and readily decomposed to inorganic HgSe species (Khan and Wang 2010). In soil–plant system, Wang et al. (2016b) suggested that Se inhibited the sulfate-mediated MeHg production in paddy soil. However, there is no conclusive evidence to confirm the in vivo conversion of MeHg to IHg in plant under Se addition up to now. Briefly, the widely accepted viewpoint by most researchers is that Hg transformation by reaction with Se to form mercuric selenide would be an effective mechanism for counteracting the potential damage of Hg to plant.

The underlying molecular mechanisms for Hg and Se antagonism in plant are complex and remain to be poorly understood. However, the following hypotheses are documented in present works:

(i) Immobilization of Hg by Se. As previously reported, a high molecular weight (above 70 kDa) Hg and Se containing compound on the root surface and in the root extract of *Brassicajuncea* was identified by Mounicou et al. (2006), in which they suggested an association of Hg with either a polysaccharide or a protein. The formation of high molecular weight (above 600 kDa) Hg and Se containing proteinaceous complex was also detected in *Glycine max* and *Allium fistulosum* (Afton and Caruso 2009; Yathavakilla and Caruso 2007). These works implied an apparent inner influence of root inclusion on the HgSe synthesis. Similar to HgS, HgSe formed in rhizosphere and root is insoluble and nonbioavailable, thus reducing the uptake of Hg and Se by root. Besides, the iron plaque locating on the root surface can restrain the uptake and transportation of HgSe and HgS from root to the above-ground parts (Li et al. 2016).

Se induced the redistribution of Hg in plant tissues based on the Hg–Se bonding. The binding strength of heavy metals can influence their movement via the root cylinder, which in turn affects their toxicity (Wang et al. 2013). Under Se amendment, the highest Se concentration in root was in the more proximal root tissues, suggesting that Se was readily loaded into the stele. This contrasted with other metal(loid)s (e.g. Mn, As) which accumulated in the apex, but similar to Hg (Wang et al. 2013; Zhao et al. 2013b). This suggests that Se–Hg bonding can readily modulate the spatial distribution patterns of Hg in plants.

(ii) The intracellular reaction of Hg and Se. In plant tissues, Hg could bound to cysteine-rich domains of the major cell wall protein extensin. With the application of SR-XRF and tomography techniques, Carrasco-Gil et al. (2011) found that the majority of Hg in alfalfa root was associated with the epidermal and endodermal tissues in the vascular cylinder. Because of the high affinity of Hg for the sulfhydryl groups, there appears a strong reaction between Hg and the cell wall which contains many thiol functional groups. In the intracellular environment, because of the abundance of thiol groups in biomolecules and their high affinity toward $Hg^+/MeHg^+$, Hg speciation in the tissues is dominated by Hg/MeHg–SR complexes. However, with the addition of Se, it could compete with thiols towards Hg binding due to the larger formation constant of Hg–SeR ($K_m = 10^{45}$) than Hg–SR ($K_m = 10^{39}$), which reduces the reactions between Hg and –SH groups in plant tissues thus preserving the regular biological activity of the –SH containing proteins (Arnold et al. 1986).

The stability and toxicity of Hg–Se compounds are largely determined by the chemical forms. Plants

such as cereals and forage crops can convert Se predominantly into SeMet and incorporate it into protein in place of methionine (Schrauzer 2003). This allows Se to be stored in the plant tissues and reversibly released by normal metabolic processes when necessary, offering advantages over other Se compounds. Under Hg and Se co-exposure, the SeMet like species stored in specific plant tissues could facilitate the interactions between Hg and Se. The potential HgSeMet analogues are responsible for the antagonism at the molecular level, i.e. bis[methylmercuric] selenide, methylmercury selenocysteinate, seleno-protein P-bound HgSe clusters, and the biominerals $\text{HgSe}_x\text{S}_{1-x}$ (Gailer 2007). The presence of these HgSe compounds in organisms has been widely indicated by direct or indirect evidence, and the chemical properties of these compounds support their critical roles in alleviating the toxicity of Hg and Se (Gailer 2007; Yang et al. 2008).

Conclusions and Perspectives

The possible in vitro or in vivo formation of unbioavailable Hg–Se compounds seems to be the most acceptable mechanisms to explain the antagonism between Hg and Se in plant. The decreased uptake and accumulation of Hg in plant, as well as the redistribution of Hg and conversion to less toxic Hg species, should be partially ascribed to the formation of Hg–Se compounds. In the laboratory experiments, the protective effects of Se against Hg phytotoxicity have been conclusively established. However, studies on the dose–effect between different Hg and Se species, as well as practical field studies are still in a great vacancy due to the various chemical forms of Hg and Se in the environment. Considering the sequestration of Hg by Se in the form of inert Hg–Se compounds, the strategy using Se to decrease Hg accumulation and enhance Se content in crops is acceptable when a comprehensive assessment of the contents and status of Hg and Se in Hg-polluted field is completed. In the mining areas, the synergistic effect between Hg and Se should also be taken into consideration. Additionally, the underlying mechanisms between Hg and Se in different plants have not yet been completely elucidated due to the complex reactive environment of various Hg and Se speciation. Given the rapid development in high-resolution analytical methods, such as the SR-based techniques, we believe that the identification and quantification of Hg and Se associated compounds in vitro and in vivo plant will become possible in the future, which will provide more plausible molecular mechanistic basis for detoxification and remediation strategies aiming to regulate Hg and Se levels in food chain.

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Compliance with Ethical Standards

Conflict of interest We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, this manuscript.

Research Involving Human Participants and/or Animals This article does not contain any studies with human participants or animals performed by any of the authors.

Informed Consent All authors of this manuscript have directly participated in planning, execution, and analysis of this work.

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