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Interaction between selenium and soil organic matter and its impact on soil selenium bioavailability: A review

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ABSTRACT

The bioavailability of selenium (Se) in soil partly determines Se deficiency in human health. Soil organic matter (OM) is an important soil component that controls Se bioavailability. Better understanding of the interaction between selenium and soil organic matter will be scientifically and practically significant in terms of Se risk assessment in the environment and Se biofortification for human health. This paper gives an overview of current understanding on the interaction between soil OM and Se in soil–plant systems, highlighting that OM can immobilize Se by both biotic and abiotic mechanisms and reduce its bioavailability, but the release of OM-immobilized Se through mineralization should not be overlooked. In addition, soil organic amendments also have diverse effects on Se bioavailability. Future research directions and challenges on this topic have been addressed.

Contents

1. Introduction

Selenium (Se), an essential trace element for humans and animals, involving multiple biological functions, such as enhancing immunization, antioxidation, and detoxification of heavy metals (Girling, 1984; Lenz and Lens, 2009; Mao et al., 2016). A low dietary intake of Se could cause various health disorders (Rayman, 2000; Tan et al., 2002). Thus, taking measures to increase Se intake by humans and animals becomes necessary in soil Se-deficient areas worldwide (Navarro-Alarcon and Cabrera-Vique, 2008; Williams et al., 2009). A daily dietary Se intake higher than 40 μg is recommended, but Se biofortification must be implemented in a way that the maximum daily dietary intake of 400 μg is not exceeded to avoid potential Se toxicity (Ellis and Salt, 2003; Fordyce, 2007; Qin et al., 2013). Because dietary Se intake is the most practical approach for Se nutrition, biofortification of Se in agriculture through Se fertilization, breeding, or genetic manipulation of crops has been proposed as an effective and safe mean to increase human Se intake (Haug et al., 2007; Winkel et al., 2015). The application of Se-enriched fertilizers can directly

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increase Se concentrations in the soil. However, it is generally assumed that only a small portion (<5%) of soil applied Se is utilized by plants (Haug et al., 2007). The effectiveness of Se fertilization depends on Se species, fertilizer dose, application technique, timing, and prevailing soil properties: the uptake efficiency can range from <1 to >50% (Mikkelsen et al., 1988; Johnsson, 1991; Tveitnes et al., 1995; Stroud et al., 2010; Keskinen et al., 2011; Kikkert and Berkelaar, 2013). The majority of the Se input was either retained in the soil or lost via soil leaching and/or surface runoff, or volatilized into the atmosphere. Water Se pollution may pose potential risks or threats to aquatic organisms (Sager, 2006). Therefore, Se bioavailability in the environment has become an important research topic.

Soil Se bioavailability varies greatly with different soil properties and composition. Soil pH and redox potential are key factors reflecting Se bioavailability. In general, Se is more strongly immobilized in acid and reductive soils (Cao et al., 2001; Johnson et al., 2000; Johnsson, 1991; Wang and Gao, 2001; Sharma et al., 2015). Among soil components, iron and aluminum minerals and soil organic matter (OM) play decisive roles in determining soil Se bioavailability (Wang et al., 2012; Weng et al., 2010; Ming-Ming et al., 2015). Earlier studies indicated that large proportions of Se species were bound/incorporated into organic and/or organo mineral colloids. Some studies documented that the Se adsorbed by minerals accounts for <20% of the total Se (Coppin et al., 2009; Selim and Sparks, 2001), and some researchers reported that the OM-bound Se fraction is up to 40–50% (Abrams et al., 1990; Gustafsson and Johnsson, 1994; Qin et al., 2012). Supriatin et al. (2015a, 2015b) reported that Se in low Se Dutch agricultural soils is predominantly in organic forms both in soil solution and solid phase, and only a small fraction (on average 5%) is present as inorganic Se (mainly selenite). These authors also found that the extractability of soil Se was highly correlated with the extractability of soil organic carbon. OM thus influences Se speciation in soils, which may have important implication for the fate of Se because these colloid-sized organic Se particles probably exhibit different mobility and bioavailability than Se oxyanions due to different chemical (e.g., functional groups, hydrophobicity) and physical (e.g., size) properties (Tolu et al., 2014b). Therefore, obtaining insight into the interaction between soil OM and Se is indispensable in studying Se bioavailability in soil.

Soil amendments with organic materials like manures and crop residues also affect the bioavailability of Se in soil. The soil organic amendments can even be applied as a method to regulate the level of soil Se bioavailability (Park et al., 2011). For instance, organic materials have been used to reduce Se toxicity in Se-contaminated soils (Dhillon et al., 2010; Sharma et al., 2011; Shrestha et al., 2006). However, the application of Se-laden organic fertilizer in soil can result in higher Se accumulation in crops (Bhatia et al., 2014; Bañuelos et al., 2015; Dhillon et al., 2007). Such biofortification practices have experienced increased research attention worldwide in recent years for the great potential of developing Se-enriched agricultural products to improve human Se nutrition and health (Bañuelos and Lin, 2010). Therefore, a better understanding of the relationship between soil OM and Se bioavailability and also of the mechanisms of the formation and transformation of OM-bound Se in soil will be scientifically and practically significant in terms of Se risk assessment in the environment, appropriate Se amendments in Se-deficient soils, and remediation in Se-contaminated soils.

For this purpose, this review focused on the interaction between soil OM and Se and impacts of OM on soil Se bioavailability. The application of soil organic amendments and future research needs on soil OM and Se chemical behaviors have also been discussed.

2. Speciation and fractionation of Se in soil

Selenium in natural environment exists in four valence states: Se(-II), Se(0), Se(IV), and Se(VI). The Se speciation in soil is basically controlled by three mechanisms: oxidation vs. reduction, mineralization vs. immobilization, and volatilization. The rate coefficients of these processes vary depending on Se species, microbial activity, pH and redox conditions, and other soil properties (Ros et al., 2016). Fig. 1 shows the dominant Se species in different pH and redox potential (Eh). Each of these compounds differ in bioavailability. Selenite (Se(IV)) and selenate (Se(VI)) are most commonly used in agricultural biofortification practices (Keskinen et al., 2011; Lyons, 2010; Peng et al., 2016; Sharma et al., 2015). Both selenite and selenate are water soluble, but selenate exhibits relatively higher water solubility and thus bioavailability than selenite in soil solution. In general, selenite is the dominant Se species under acidic and reducing conditions in humid areas (Allaway, 1968), which tends to form strongly bonded inner-sphere complexes on metal oxides surfaces (Brown et al., 1999) or soil organic matter (Levesque, 1974) and shows low bioavailability. In contrast, Se tends to be more bioavailable in well-aerated alkaline soils where it occurs as selenate, which is subject to leaching from soils through runoff. Hydroponic experiments have shown that plants preferred selenite over selenate when the same amount of these two inorganic Se compounds was compared (Hawrylak-Nowak et al., 2015; Longchamp et al., 2013; Versini et al., 2016). Elemental Se [Se(0)] and metallic selenides [Se(-II)] are water insoluble and cannot be directly utilized by plants (Fernández-Martínez and Charlet, 2009). However, Se in organo-Se compounds (e.g. seleno-aminoacids), present a valence of −2, are highly bioavailable. Se accumulation in plants is higher when seleno-amino acids are added to the hydroponic growth medium compared with inorganic forms of Se at the same concentration (Kikkert and Berkelaar, 2013). As such, seleno-amino acids may be an exceptionally active component in organic Se fertilizers and can be added to the soil through the application of Se-amended organic fertilizers (Bañuelos et al., 2015; Eich-Greatorex et al., 2007). Besides, organo-selenium compounds can also be released into the soil from biological decomposition of plant and soil microbial tissues (Chasteen and Bentley, 2003).

Selenium compounds can be adsorbed by different soil components and distributed differently among various soil fractions. A disparity in terms of bioavailability can be found in different chemical fractions of Se in soil. Based on their binding strength and fractionation extractability, soil Se can be allocated into the following five fractions: water soluble Se, exchangeable Se, iron (Fe)/manganese (Mn) oxide-bound Se, OM-bound Se, and residual Se (Hu et al., 2014; Wang and Chen, 2003; Wang et al., 2012; Wang et al., 2016). Selenium in different fractions displays various degrees of mobility and bioavailability. Water soluble and exchangeable Se are free in soil solution or weakly

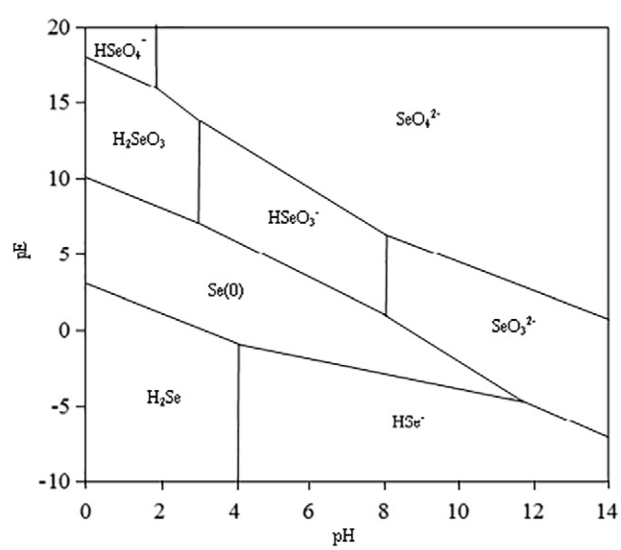

Fig. 1. Selenium pE–pH diagram at 25, 1 bar pressure and 0 ironic strength for a dissolved selenium activity of 10^{-10} mol L^{-1}.
(Cited from Séby et al. (2001).)