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Status and risks of selenium deficiency in a traditional selenium-deficient area in Northeast China

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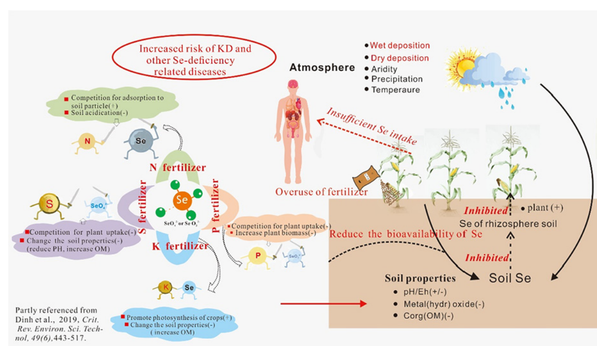
HIGHLIGHTS

- Fertilizers impede the soil-to-plant migration of Se in the adjacent soil rhizosphere.
- Climate conditions, soil properties are the key factors influencing the spatial distribution of soil Se.
- The bioavailability of Se levels in plants should be noticed to prevent underestimating the potential risk of Se deficiency under applying conventional fertilizers.

GRAPHICAL ABSTRACT



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ABSTRACT

In agricultural lands with selenium (Se) deficiency, bioavailability of Se in plants is low. Residents from large-scale agricultural production areas with Se deficiency often suffer from endemic diseases because of consumption of agricultural products lacking in Se. One such area in Northeast China where Keshan disease and Kashin–Beck disease originated, was selected for investigating the geochemistry, influencing factors, and risks of Se in the agroecosystems. Analysis of field samples indicates that the Se deficiency in soil is significantly reduced compared with that of several decades ago, and 62.6% of soils are now Se-sufficient in the southern Songnen Plain. However, Se in crop products remains low due to weak soil-plant transfer, resulting in high risks of Se deficiency related diseases in the rural population of this area. Structural equation modeling, principal component analysis, and other statistical analyses revealed that climate conditions and soil physical and chemical properties are the key factors influencing the spatial distribution of soil Se. Extensive use of agricultural fertilizers may indirectly inhibit the migration of Se from soil to plants. Ensuring sufficient Se contents in agricultural products to meet the minimum daily requirements of residents remains a challenge in Se-deficient areas, especially in the increased agricultural production environment in China.

1. Introduction

Selenium (Se) is an essential, two-sided micronutrient for human health. Selenium is closely related to the physiological functions of the human body, and a lack of Se can lead to a variety of diseases (Amaral

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et al., 2008; Hao et al., 2016). Se plays essential roles in energy metabolism and gene expression (Zhang et al., 2014). There are two main kinds of Se, i.e., those containing amino acids and those containing proteins (Bailey, 2016). Se occurs as an essential micronutrient in the form of selenoproteins, selenocysteine, and selenomethionine, which influence important biological functions, such as free radical metabolism, immune function, and apoptosis (Clark et al., 1996; Rayman, 2000; Taylor et al., 2009). Se deficiency is thought to be responsible for the widespread prevalence of cardiomyopathy, which is widely linked to a Se intake of <10 μg/day (Dinh et al., 2018). An insufficient Se intake in humans is also linked to Keshan disease (KD) and Kashin–Beck disease (KBD) (Fordyce, 2005; Shi et al., 2016). KD is an endemic disease mainly caused by cardiomyopathy, and KBD is a local chronic symmetric osteoarthropathy (Yao et al., 2011; Zhang et al., 2014). Se mainly exists in organisms in the form of organic Se compounds (Borella et al., 1996), and protects tissues from oxidative damage by increasing the activity of Se proteins on the whole (Rayman, 2000; Yiyong et al., 2002). In addition, environmental geological studies have shown that the incidence and mortality of tumors are negatively correlated with the geographical distribution of Se (Alloway, 1995). Symptoms of cognitive impairment may show up in people with chronic Se deficiency and the incidence and mortality of tumors in low-Se areas are higher, and the Se levels in tumor patients are lower than those in healthy people. When Se intake is insufficient, the brain is the last organ to show a decrease in Se concentration, and chronic Se deficiency can lead to cognitive impairment (Hao et al., 2016; Steinbrenner and Sies, 2009).

The Se level in the human population depends on long-term daily intake, as soil is not only the main source of Se in crops, but also influences the total amount of Se accumulated in humans through the food chain (Antoniadis et al., 2017; Dinh et al., 2019; Zhang et al., 2014). However, the spatial distribution of Se in soil is heterogenous and variable. Globally, it predominantly ranges from 0.01–2.0 mg/kg, with a mean value of 0.4 mg/kg; however, soil Se can reach up to 1200 mg/kg in high geological background areas (Dinh et al., 2018). In China, Se is typically deficient in surface soils, and approximately 51% of soil is estimated to be below or close to the deficient level (0.125 mg/kg) (Dinh et al., 2018, 2017, 2019). Minimum and maximum Se concentrations and Se fluxes have been reported previously in different environmental media in China (Zhu et al., 2004, 2008). Se-deficient areas primarily include the low-Se geological belt that extends from the northeastern to southwestern regions of China, including northeast China, the Taihang mountain ranges, the Qinling mountain ranges, the Loess Plateau, and the eastern region of the Tibetan plateau, where Se contents in soils are <0.125 mg/kg (Chen, 2012; Li et al., 2012; Panchal et al., 2017; Yao et al., 2011). However, endemic selenosis also occurs in areas with a high Se concentration in the soil derived from locally Se-rich parent material (Li et al., 2012; Zhu et al., 2004), such as Enshi in Hubei province and Ziyang in Shaanxi province, where soil Se contents are as high as 79.08 mg/kg and 36.69 mg/kg (with means of 27.81 mg/kg and 17.29 mg/kg), respectively (Tian et al., 2016; Yuan et al., 2012). Research conducted in varying Se level areas has indicated that the content, distribution, bioavailability, and ecological effects of Se in China are complicated (Chang et al., 2019; Zhuang et al., 2009). As such, it is difficult to assess the health risks associated with Se deficiency and toxicity. Existing studies on the response of the Se concentration in soil to environmental factors mainly focus on natural environmental factors and the anthropogenic inputs by mining and smelting industries (Barron et al., 2012; Blazina et al., 2014; Dinh et al., 2019; Fakour et al., 2016). The patterns of soil-plant Se dynamics over China's major agricultural production regions may be site-specific because of the various climate conditions and distinctive fertilizer usage (Dinh et al., 2017). Currently, only a few studies have paid attention to Se in the agricultural ecosystem, especially in areas that were once at a high risk of Se deficiency which increased the risk of various endemic diseases, such as KD and KBD, and weakened the antagonistic effect of Se and other toxic substances, increasing the risk of exposure to other harmful substances in the human body (Dinh et al., 2019; Garcia et al., 2013).

Endemic diseases (KD and KBD) exhibit high prevalence in the southern Songnen Plain, which belongs to the low-Se geological belt straddling the Se-deficient and Se-marginal areas in Northeast China and is where KD originated. With the highest grain output in the world for 10 consecutive years, China's grain output is now close to 664 million tons, which is approximately 24.4% of the total global grain output. Besides, Heilongjiang province is China's largest province in terms of grain yields and cultivated areas (for the seventh consecutive year), contributing approximately 11% and 9.7%, respectively (National Bureau of Statistics of China, 2020). The southern Songnen Plain accounts for 48% of Heilongjiang's total grain outputs. To date, the problem of health risks in "quondam" Se-deficient areas after the implementation of numerous corrective measures has received scant attention from researchers (González-Morales et al., 2017; Harris et al., 2014; Jones et al., 2017; Tan et al., 2002). In order to explore the current status and the associated health risks of Se deficiency in China's most important grain production base, we performed field experiments and statistical analyses of Se in soil and crops. Hence, the objectives of this study were to: (1) assess whether the Se level is elevated in typical areas; (2) discriminate and quantify factors and causes that affect the Se levels, and; (3) assess the health risks of direct consumption of locally grown food.

2. Materials and methods

Detailed information of the sampling site, sampling methods, analytical method, statistical analysis, etc. in this study is provided in the Supporting Information (SI Materials and methods).

2.1. Sampling and analytical methods

A total of 20,929 surface soil samples (to approximately 0–20 cm depth) and 1440 deep soil samples (to approximately 200 cm depth) were collected from the southern Songnen Plain between 2010 to 2013 (Fig. 1). Additionally, 36 corn kernel (*Zea mays* L.) samples, including the corresponding rhizosphere soils, were collected from cropland in Gannan County, located in the northwest of the Songnen Plain (Fig. 1).

After the soil was air-dried and passed through a 200-mesh sieve, a 50-mg aliquot was digested with a mixture of HF, HNO_3, and $HClO_4$ at a ratio of 5:5:1 and heated at 180 °C until the solution became transparent. X-ray fluorescence spectroscopy (XRF) was used to detect CaO, K_2O, MgO, Na_2O, Al_2O_3, TiO_2, Fe_2O_3, MnO, B, P, Zn, Cu, Cr, Ni, and Pb in the obtained solutions, whereas inductively coupled plasma mass spectrometry (ICP-MS) was used to analyze Mo, Co, and Cd. Hg and Se were determined via atomic fluorescence spectrometry (AFS). The detection limit of Ca, Mg, Fe, Hg, Co, Pb, and Cd was <0.1 μg/L, the detection limit of K, Na, Al, Zn, Cu, Cr, Mn, and Ni was 0.1 μg/L, the detection limit of P was 1 μg/L, and that of Se was 0.01 μg/L.

For Se analysis in soil and corn kernel, a mixture of HNO_3 and $HClO_4$ (5:1) was added and heated at 180 °C until the solution became transparent. This mixture was used for the detection of Se and As via hydride generation atomic fluorescence spectrometry (HG-AFS) (Boyle, 1981; Page et al., 1982) with a detection limit of 0.01 μg/L. The soil As content in the study area was also tested by a method similar to Se (Lin et al., 2020). The pH and organic matter (OM) content of the soil samples were determined by the glass electrode method and titration method, respectively (Ahmad et al., 2017). A standard extracting solution method from US-EPA (1986) was used to determine the cation exchange capacity (CEC) of the soil. Total organic C (TOC) was measured with an elemental analyzer (Euro Vector) (Wang et al., 2003). Sulfur and N were determined via dry combustion (at 1350 °C) with a LECO

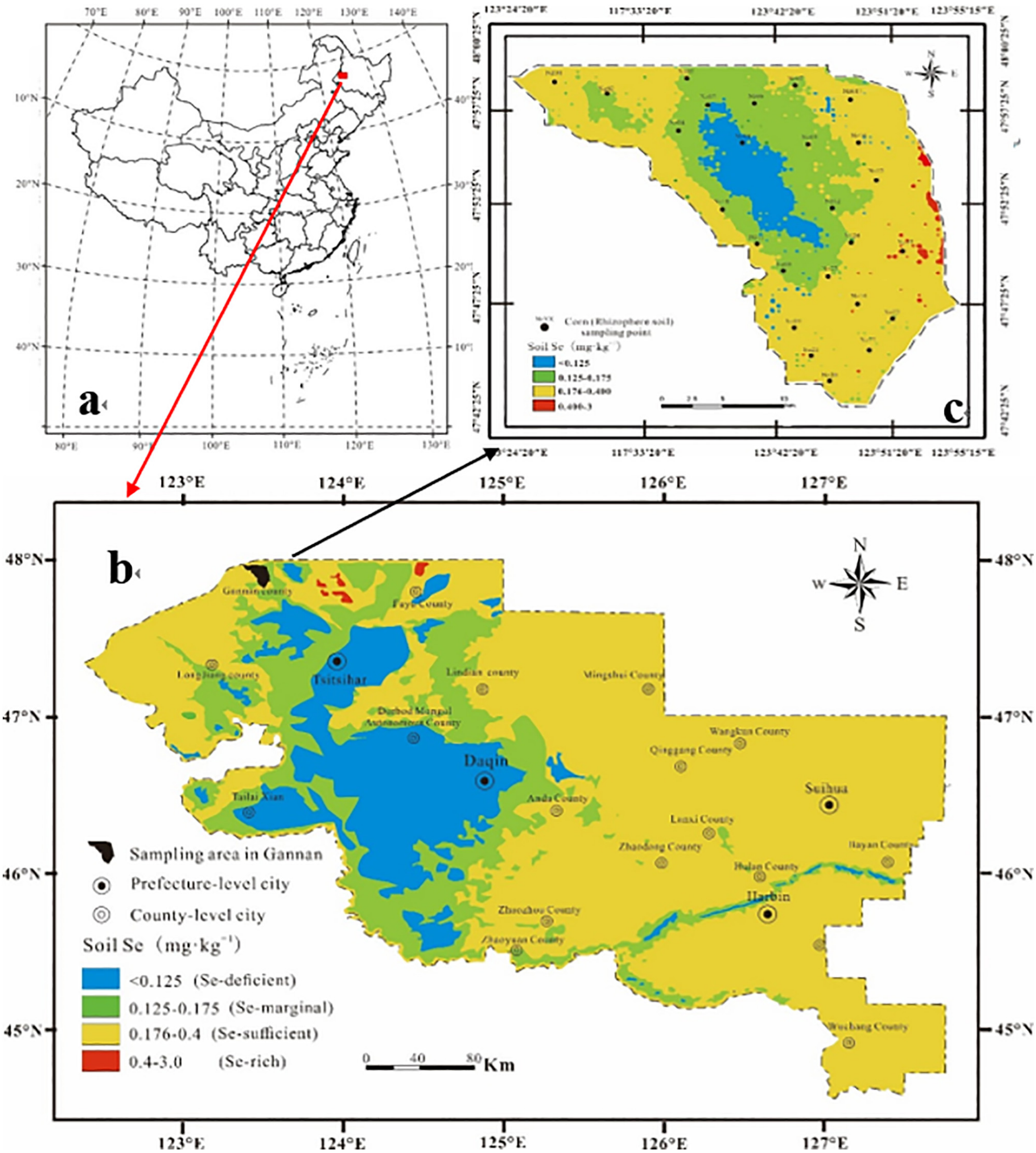

Fig. 1. (a) Location of the study area in China, and the distribution of soil Se in (b) Songnen Plain and (c) Gannan county.

CNS-2000 analyzer. SiO_2 was determined via XRF analysis (Hönicke et al., 2012).

In this study, the availability of elements/compounds in the soil-plant system was determined for ammonium ion ($NH4^+$), Olsen P (A-P), available K (A-K), available B (A-B), available Mo (A-Mo), available Cu (A-Cu), available Fe (A-Fe), available S (A-S), and available Zn (A-Zn), following the method of LY/T 1210-1275 (Administration, 1999). Se fractions in soil have been classified into water-soluble Se (SOL-Se), ion-exchangeable Se (EXC-Se), organic Se (OM-Se), carbonate Se, and residual Se fractions. Apart from some fulvic acid bound Se (FA-Se) with low-molecular-weight forms of OM-Se, water-soluble Se, ion-exchange Se and carbonate Se are defined as bioavailable Se in soil in the existing studies (Dinh et al., 2019; Gao et al., 2011). Se speciation and availability in soils were determined with the procedures are supplied in SI 1.

2.2. Statistical analysis

In this study, all soil data collected in Gannan County, including climate, biotic, and edaphic characteristics, were subjected to Box–Cox transformation to meet the assumptions of normality by R programming software (Supporting Information; SI 2). Based on the Pearson correlation analysis, we then established a structural equation model of climate (precipitation, temperature, near surface evaporation

[NSE]), nutrient element contents (N/P/K/S), soil Mn/Fe/Al, soil properties, and soil Se, which are all important factors affecting the Se concentration in soil (Antoniadis et al., 2017; Dinh et al., 2018, 2019; Ham and Tamiya, 2006; Muller et al., 2012; Shaheen et al., 2018). Then, a principal component analysis (PCA) was performed to obtain multivariate functional indices representing the impacts of these factors on soil Se concentrations (more details are provided in the Supporting Information Table S2). All indexes were standardized into *Z*-scores. To make the data more convenient for later analysis, we removed the union set of abnormal data (106/2151) from the Gannan region according to the three-sigma rule prior to modeling. Then, structural equation modeling was developed from the conceptual model using χ^2 tests with maximum likelihood estimation. Model fitting was performed using SPSS 21.0 and Amos software 21.0. We used *p*-values (>0.05), χ^2 values, and degrees of freedom (df) as criteria to evaluate the structural equation modeling fit. In path network analysis, the standardized path coefficient (β, where values closer to 1 represent a stronger influence) represents the direct effect of one variable on another; the indirect effect (e.g., where one variable affects another variable, which in turn affects a third) was calculated by multiplying each associated β value (Wang et al., 2019).

2.3. Index of health risk assessment

To estimate the human exposure risk of Se through daily diet, the probable daily intake (PDI) was calculated for the adult population of the southern Songnen Plain using the following equation:

$$PDI = \sum \left(C^i \times IR^i\right)/bw,$$

where *C* is the total Se concentration of the exposed medium (mg/kg); *IR* is the intake rate (the rate of ingestion or inhalation), and *i* is the intake of a potential daily diet derived from the results of Chen et al. (2011) and corn kernel samples collected in this study.

3. Results and discussion

3.1. Se characteristics of soil in the southern Songnen Plain

Selenium in topsoil (0–20 cm) of the southern Songnen Plain varied from 0.01–1.14 mg/kg, with an arithmetic average of 0.29 mg/kg and a coefficient of variation of 38%. The average value is clearly lower than the national average (0.4 mg/kg); however, it is 15% higher than that reported by He and Zheng (2008) for the same area, suggesting that the Se content in the surface soil of the southern Songnen Plain has increased slightly over the last decade (Table S1).

Four classes of soil Se were previously defined by Tan et al. (2002) based on the soil Se content, namely, Se-deficient (<0.125 mg/kg), Se-marginal (0.125–0.175 mg/kg), Se-sufficient (0.176–0.4 mg/kg), and Se-rich (>0.4 mg/kg). As shown in Fig. 1, the areas in the southern Songnen Plain were predominantly Se-sufficient (62.60% of total area), followed by Se-marginal (17.55%), Se-deficient (16.89%), and Se-rich (2.96%). In the southern Songnen Plain of the studied area, the distribution of Se in the topsoil has obvious aggregations, as shown in Fig. 1b. The aggregation of the "cold spot" with Se-deficient areas mainly appears around Qiqihar and Daqing, where there has been a focus on industrial development over the past several decades. Conversely, similar to the densely populated cities, the soil Se level of Harbin and Suihua is Se-sufficient. Furthermore, the soil of other non-populated township areas generally exhibited Se-sufficient or even Se-rich characteristics. In addition, most of the Se-marginal areas are in the northern part of the study area, on the edge of the "cold spot", which usually play the role of buffer zone between Se-sufficient areas and Se-deficient areas. The cause of this uneven distribution is the Se supplementation during the agricultural planting process, whereas the area in which the "cold spot" is located has a less obvious uneven Se distribution due to long-term industrial production. A low level of Se (average 0.112 mg/kg) caused by geological factors was retained in the deep soil (Fig. S1). There was a weak spatial correlation between the surface soil Se level and the deep soil Se level. The deep soil Se content in Suihua and other areas in Harbin was at a medium level with a relatively high Se level in the deep soil. This indicated that the Se level of the surface soil is mainly determined by external factors in addition to its inheritance from the original soil Se level.

As a major grain production base in northeast China, the southern Songnen Plain may be affected by agricultural production, and the content of the surface soil Se in the southern Songnen Plain is higher than the average content of the whole Heilongjiang province (0.147 mg/kg) (Xu et al., 2016), which is similar to the average value of soil Se in the adjacent Jilin province (0.2 mg/kg) (Fu et al., 2014). Compared with the other main grain production areas worldwide, the risk of a low-Se level in the cultivated soil on the Songnen Plain limits the development of a high-quality agricultural industry, despite the considerable scale of the grain yield in the south of the Songnen Plain. Except for several large grain-producing areas with relatively weak agricultural technologies (e.g., Romania (Tamás, 2015) and West Siberia (Aleksandrovskaia et al., 2020)), the soil surface Se content in the major grain-producing areas of developed countries (such as southern Scotland (Fordyce, 2013) and the central United States (Fordyce et al., 2009)) has reached a Se-rich level.

The ratio of the Se content of the surface soil to that of the parent material was close to 1.8–2.9 in southern Songnen Plain soil, whereas the average total Se of the deep soil (at a 200-cm depth) was less than that of the C-layer soil in Eastern China with an average of 0.1 mg/kg generally (National Bureau of Statistics China, 2010). The similar Se content distribution in vertical soil profiles did not appear in other areas (Xueqi et al., 2012), such as Yaoxian and Chuxiong, where the surface soil is Se-deficient or Se-marginal, suggesting that Se has obvious surface aggregation characteristics in the soil of the Songnen Plain (Dinh et al., 2018). However, according to the relevant dry subsidence study of the Songnen Plain, the amount of Se in the atmospheric dry subsidence in the study area cannot primarily explain the distribution characteristics in the soil profile indicating that the soil is greatly affected by anthropogenic inputs (Xueqi et al., 2012; Yang et al., 2019). In addition to inheriting the parent material, it is also possible that imports from other sources have played a crucial role in the surface aggregation of soil Se on the southern Songnen Plain in recent years (Xueqi et al., 2012).

Interestingly, at the northern edge of the study area (Fuyu County and Gannan County), a small amount of Se-rich surface soil is distributed in about 845.6 km^2. Previous studies on the soil profile in the Songnen area speculated that there is a large amount of Se (up to 1.86 mg/kg) bound with OM materials in the Upper Carboniferous black slate, sandy and other sedimentary rocks rich in organic material under the soil with thinner soil systems developed (<50 cm) (Li, 2017). It indicates that most of the area is covered by quaternary sediments poor in Se, with a Se content as low as the parent soil, thus leading to a lack of Se supply from deep rocks for most of the surface soil. This may partly explain the present situation of Se in the Songnen Plain top soil.

3.2. Se speciation in soils

Bioavailability, despite being used widely in the literature, is a concept that has not been defined generically (Dinh et al., 2019). Se in soil mainly exists in four different oxidation states, namely, Se (II), Se (0), Se (IV), and Se (VI) (Stasinakis and Thomaidis, 2010). Se (IV) is less soluble and bioavailable than Se (VI) (Peng et al., 2016). Thus, bioavailable Se is defined as the freely available Se transported from soil to the cellular membrane of a plant (Dinh et al., 2019). The concentration of bioavailable Se obtained from the samples collected in the present study ranged from 0.001–0.049 mg/kg, with an average of 0.00928 mg/kg. The proportion of the bioavailable Se to the total Se ranged from 1.92–38.7%, with a mean of 4.7%, which was lower than that determined in previous studies (Jia et al., 2018; Xu et al., 2018) (Fig. 2). Se species strongly bound with organic compounds accounted for the largest proportion of the total Se (approximately 24.37–56.25%), followed by humic substance-bound Se (HA-Se), which accounted for 18.21–52.12%. HA-Se in soil is stable and does not easily decompose (Dinh et al., 2017; Supriatin et al., 2015). Therefore, Se in soil of the southern Songnen Plain may not be readily absorbed by plants. Fig. 2 shows the relationship between the total Se content and the water-soluble Se content in soils indicating a significantly positive relationship between these two factors ($r = 0.47$, $p < 0.01$) and suggesting that the total Se content in soil is one of the determining factors of the soluble Se content in soil. Hence, total Se in soil of the studied area can be used to evaluate the Se bioavailability in soil, which plays an important role in controlling Se concentrations in plants (Dinh et al., 2018).

Fig. 3 shows that the available Se content in the soil increased with an increase in the total Se content. When the total Se content was >0.05 mg/kg, the ratio of the available Se to the total Se was

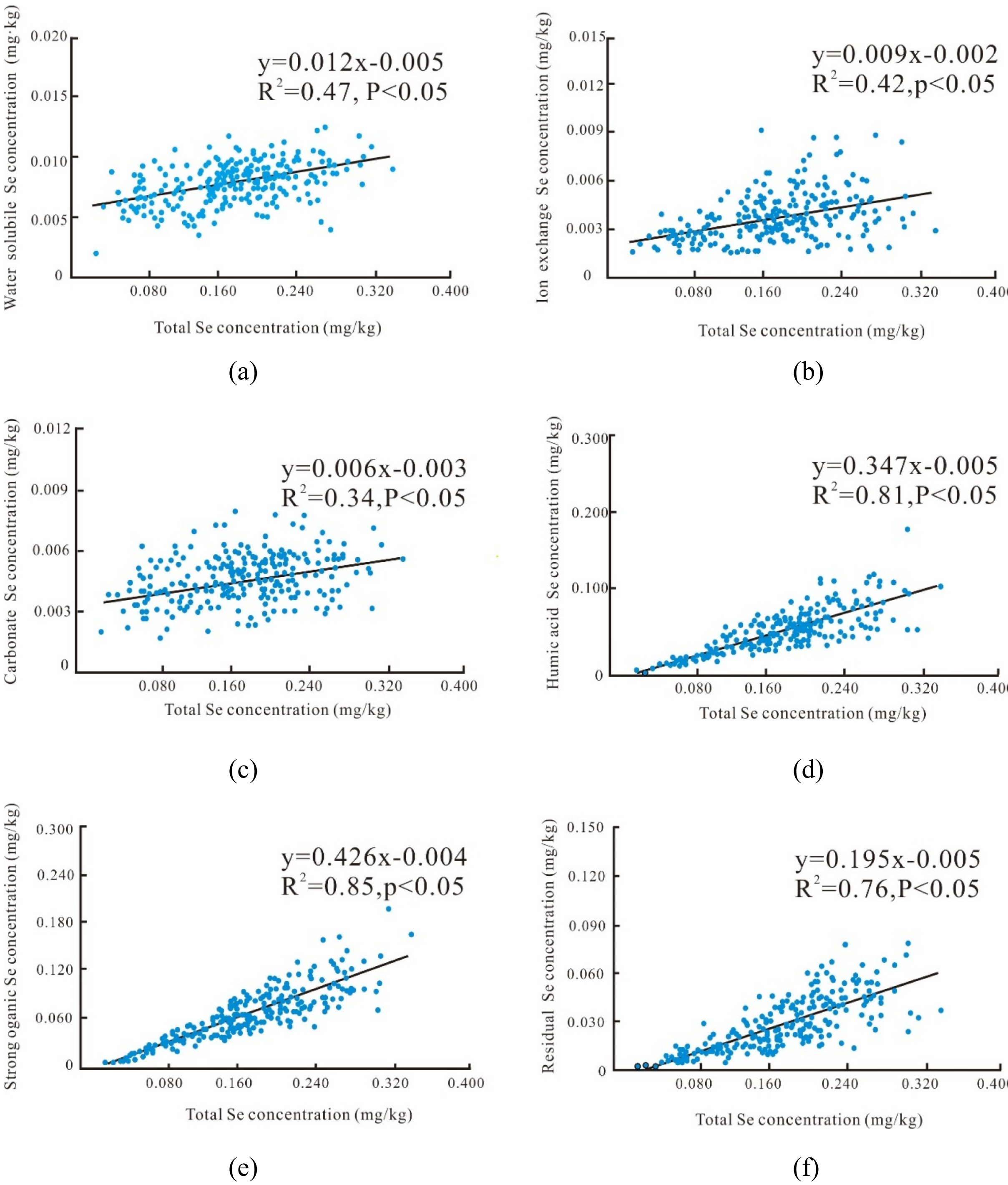

Fig. 2. (a) Correlation between water-soluble Se and total Se in soil, (b) correlation between ion-exchangeable Se and total Se in soil, (c) correlation between carbonate Se and total Se in soil, (d) correlation between humic acid Se and total Se in soil, (e) correlation between strong organic Se and total Se in soil, and (f) correlation between residual Se and total Se in soil ($n = 266$).

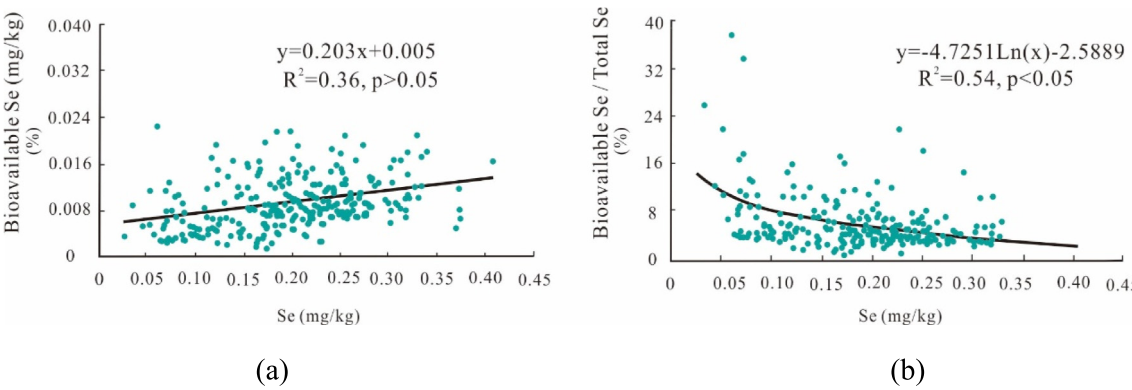

Fig. 3. (a) Correlation between bioavailable Se and total Se in soil, and (b) correlation between the proportion of bioavailable Se/total Se and total Se (n = 266).

approximately stable at 4.7%. When the total Se content increased from 0.05 to 0.2 mg/kg, the ratio increased rapidly with the decreasing total Se content (Wang et al., 2017). This result may be explained by the fact that the content of the bioavailable Se in soil is not affected only by the total Se.

3.3. Impact of soil properties on Se in soil

The soil Se distribution can be affected by different chemical processes, such as pH, redox potential, OM content, and the presence of other competitive ions (Dinh et al., 2018). Parent materials also have a primary effect on the Se content of the top soil, apart from inputs by human activities, especially in Se-toxic areas (Fordyce et al., 2000; Hartikainen, 2005; Wang et al., 2017; Wang and Gao, 2001).

3.3.1. Effects of total organic carbon (TOC) on Se content

Soil organic compounds have two contrasting effects on Se mobility and bioavailability in soil (Dinh et al., 2017) and play a key role in regulating the bioavailability of Se. To some extent, TOC has a large specific surface area and a strong chelating ability (Fakour et al., 2016). The structures and characteristics of TOC determine its effect on Se bioavailability (Supriatin et al., 2016). Wang and Gao (2001) observed a negative correlation between TOC and Se bioavailability in 16 different soils in China with various physicochemical properties. In contrast, Se bioavailability is promoted under low pH and high OM conditions (Dinh et al., 2017, 2019; Sharma et al., 2015). This dual effect of soil TOC on Se availability is due to the fact that high-molecular-weight organic acids chelate with Se in soils, reducing its mobility, whereas low-molecular-weight organic acids can dissolve and release Se that is immobilized onto the soil solid phases (Coppin et al., 2006; Dinh et al., 2018, 2017, 2019; Sharma et al., 2015).

As shown in Fig. 4, except for HA-Se, the ratio of the HA-Se concentration to total Se increased with increases in the pH. The influence of pH on the Se content differed for the Se content in different fractions, which are regarded as the bioavailable Se, in the following order: SOL-Se > carbonate Se > ion-exchange Se. Previous studies on the dominant soil types in China have demonstrated that pH has a negative effect on Se adsorption in soil, i.e., Se adsorption decreases with increasing pH (Li et al., 2016; Wang et al., 2017). As the main type of bioavailable Se, SOL-Se is the most mobile fraction and can be easily absorbed by plants (Kamei-Ishikawa et al., 2007). However, HA-Se, which is stable, difficult to decompose easily, and has a negative linear dependence on pH (Kamei-Ishikawa et al., 2007), was detected more in acid soils than in alkaline soils. Indeed, Se bioavailability was reduced under low pH and high humic acid conditions (Dinh et al., 2017). Compared with HA-Se, the various bioavailable forms of Se showed a similar downward trend with the increase of TOC. The HA-Se content showed a stable or fluctuating trend with the increase of TOC in soil (Fig. 4g and h). The results indicated that TOC had a negative impact on the bioavailability of soil Se on the southern Songnen Plain, while there was no obvious correlation between HA-Se and TOC.

3.3.2. Effects of phosphorus (P) and manganese (Mn) on Se content

In this study, the soil samples were divided into four types according to the soil types (saline-alkali, alluvial, paddy, and chestnut soils), all of which can be classified in the neutral to alkaline soil range. The Se contents in the samples exhibited a positively linear relationship with the P contents with a wide range of values (Fig. 5). The increase in soil Se with the increase of P was the most rapid in the saline-alkali soil (Fig. 5a), followed by the chestnut soil and the alluvial soil (Fig. 5b and d). The P content in the paddy soil was 2–3 times higher than that in the other three soil types, which ranged between 500 and 1500 mg/kg (Fig. 5). Inorganic P in soil accounts for 50–80% of the total P content, and the majority exists as slightly soluble compounds (Hinsinger, 2001; Mader et al., 2002). In neutral and alkaline soils, the main inorganic P is calcium or magnesium phosphates, with the former occurring in larger amounts than the latter (Hinsinger, 2001). Calcium phosphate (phospholimestone) readily adsorbs Se (IV), but absorbs minimal Se (VI) (Dinh et al., 2018). The observed increase in soil Se with P concentrations may be attributed to phosphate conversion. Phosphate can influence Se sorption on the soil surface since orthophosphate anions are able to readily displace the sorbed Se from the clay mineral and OM surface and compete with Se for inner surface complexation sites on the soil surfaces (Alloway, 1995). The presence of phosphate may decrease the Se sorption on the soil surface and increase the Se concentration in the soil solution (Dinh et al., 2018). Excessive application of P in agricultural soils may inhibit Se accumulation in plant roots with lower selenite levels, but not in those with higher selenite levels (Hinsinger, 2001). Another source of uncertainty is that the phosphate fertilizer applied to agricultural land at the same time acts as the external input source of soil Se. Previous conditional control experiments revealed that differences in the Se content were influenced by P rates in the soil but exhibited no significant correlation (positive or negative), although the relationship was statistically significant at different Se levels (Fang et al., 2003; Huang et al., 2017; Sharma et al., 2015).

Due to their extensive chelating ability and specific surface area, Mn/Fe/Al oxides also play key roles in the adsorption process (Muller et al., 2012). Fig. 6 provides an overview of a linear correlation between soil Se of weak alkali-alkaline soil or oxidized soil and their MnO content. The soil Se content increases with increasing MnO content, exhibiting a significant linear relationship. Fe/Al/Mn oxides are regarded as the major factors affecting the adsorption process because of their extensive chelating ability and specific surface area (Dinh et al., 2019). Some fractions in the soil, such as amorphous material Se, carbonate-bound Se, FA-Se, and Mn/Fe/Al oxide-Se, are defined as potentially bioavailable Se at any given moment in soil, which can be exposed to a reversible pool or the plant roots under certain conditions (Dinh et al., 2019). In contrast, amorphous iron hydroxide is able to bind with Se, indicating

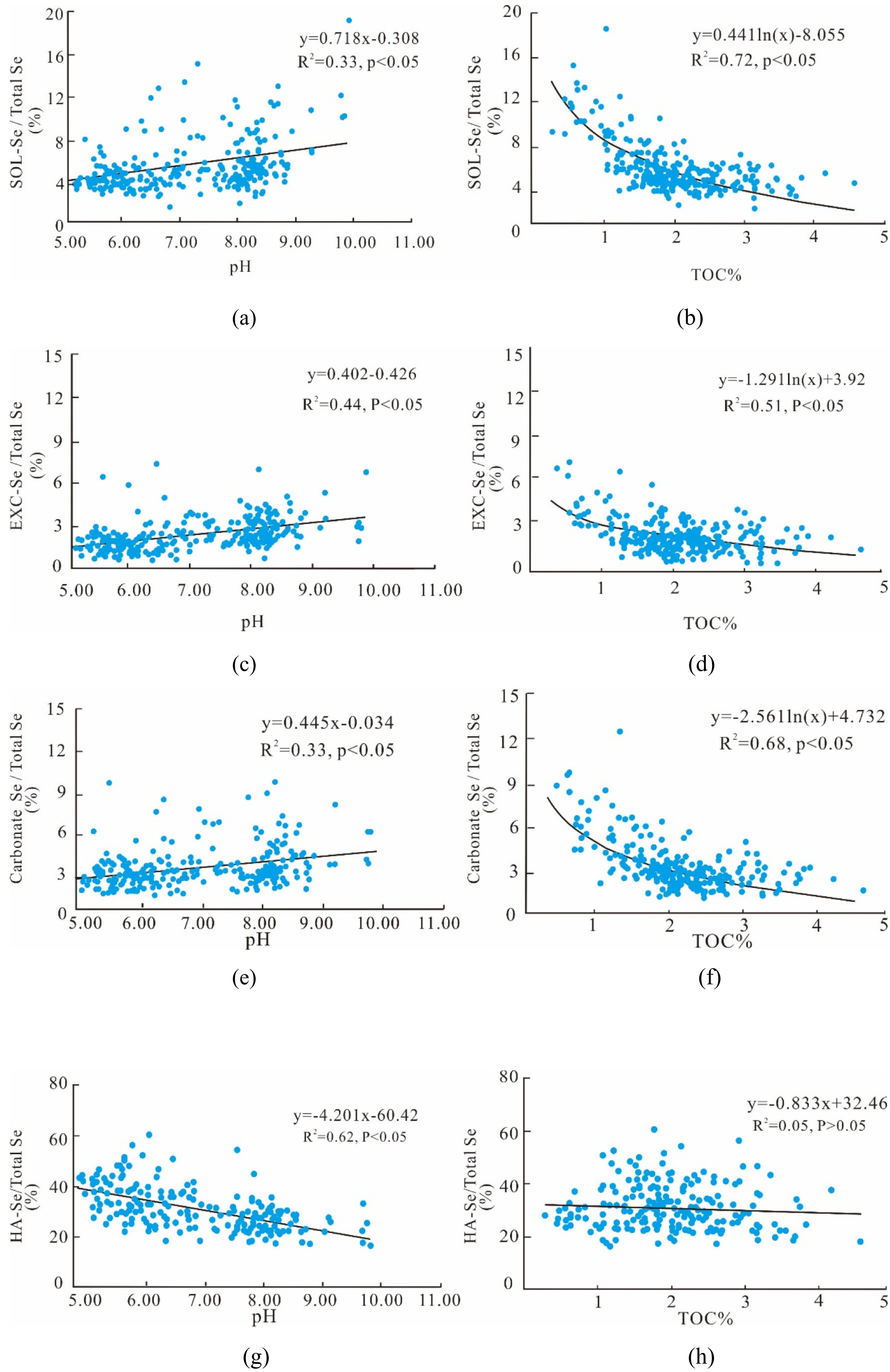

Fig. 4. Correlations between pH, total organic carbon (TOC), and bioavailable fractions of soil Se in different fractions (n = 266).

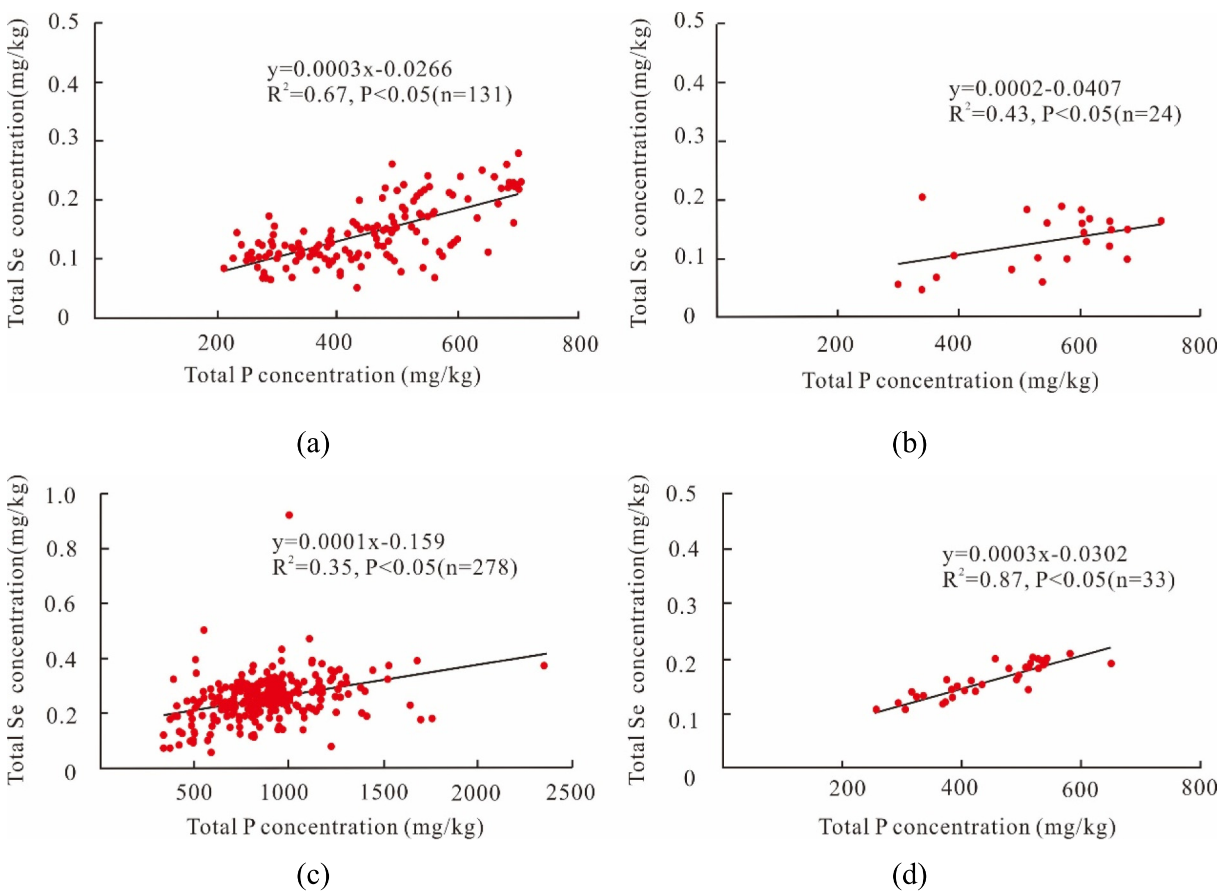

Fig. 5. Correlation between P and total Se in different soil types, (a) saline-alkali soil, (b) alluvial soil, (c) paddy soil, and (d) chestnut soil.

that Se bioavailability is reduced in the 18 types of Chinese soils (Feng et al., 2016).

3.4. Principal component analysis with respect to total Se and influencing factors

In order to explore the factors influencing the Se content in crops in the southern Songnen Plain, corn (*Zea mays* L.) (Table S3) was sampled from Gannan County, which has a typical agricultural economy, and whose input of Se is the lowest of all regions of the southern Songnen Plain (Xueqi et al., 2012). PCA was conducted with respect to total Se and other trace elements to identify the possible sources of soil total Se. According to their eigenvalues (>1), the first three principal components, accounting for 59.71% (PC1), 16.89% (PC2), and 8.21% (PC3) of the total variance, respectively, were retained for further analysis as they explained a cumulative variance of 84.81% (Fig. 7).

PC1 was characterized by a combined source of atmospheric deposition and vehicle emissions. Trace metals with high loadings in the same principal component were assumed to share a similar origin. Cu, Cr, Ni, Co, Zn, Pb, As, and Mn had positive loadings on PC1. As the studied area is located in the most active sandstorm area of China, atmospheric deposition is still deemed a potential source of Pb, As, and Ni in agricultural soils (Gupta et al., 2014; Hou et al., 2014; Tian et al., 2016). Moreover, Cu-Zn-Pb pollution was attributed to vehicle emissions (Sun et al., 2013). Additionally, Zn and Cu may be added to the local cattle diet to enhance the immunity of livestock (Sun et al., 2013). The existence of Cr in PC1 also testifies to the characteristics of source input of atmospheric deposition, which is derived from mixed sources, including phosphate fertilizers, sewage sludge, and atmosphere deposition in agricultural land in England (Nicholson et al., 2003).

PC2 exhibits a strongly positive correlation with Hg and Se (Fig. 7). The coexistence of Se and Hg in various organisms and ecosystems has been recognized in previous research (Dinh et al., 2018; Terry et al., 2000; Zhang et al., 2014), whose binding affinity (10^{45}) is one million times higher than the binding affinity (10^{39}) of mercury sulfide (HgS) (Khan and Wang, 2009). Furthermore, during the interaction of Se and Hg, metabolically inert HgSe precipitates are formed, which have a substantially lower solubility (10^{-58} to 10^{-65}) than HgS and a negative influence on the Se absorption of crops from soil (Zhang et al., 2014). For the corn crops in the studied area, a positive correlation was observed between Hg concentrations and Se concentrations in cultivated soil near the corn sample ($R^2 = 0.52$, $p < 0.01$; log-transformed) and in the corn root soil ($R^2 = 0.75$, $p < 0.01$; log-transformed). However, no similar correlation was observed for the edible part of the corn, indicating that insoluble Hg-Se complexes are produced in the rhizosphere and/or root, which is consistent with the results for rice paddy ecosystems in Hg-contaminated areas from a previous study (Zhang et al., 2014). The results are similar to those of a previous study (Fig. 7) (Sun et al., 2013).

PC3 is primarily characterized by Cd and Mo (Fig. 7), which have similar sources in farmland. Chemical fertilizer applications lead to the inputs of Cd and Mo into agricultural soil and these elements can be atmospherically deposited onto farmland soil from coal burning residues generated by industrial facilities around the research area (Cabrerizo et al., 2020; Shao et al., 2013). Therefore, PC3 mainly represents coal combustion and fertilizer sources.

The results of PCA based on Se and soil physicochemical properties are shown in Fig. 8, which indicate a cumulative variance of 78.54% for the first four principal components, with values of 33.28%, 20.41%, 13.52%, and 11.34% for PC1, PC2, PC3, and PC4, respectively. PC1 was positively related to total Se, soil organic C (Corg), available S (A-S),

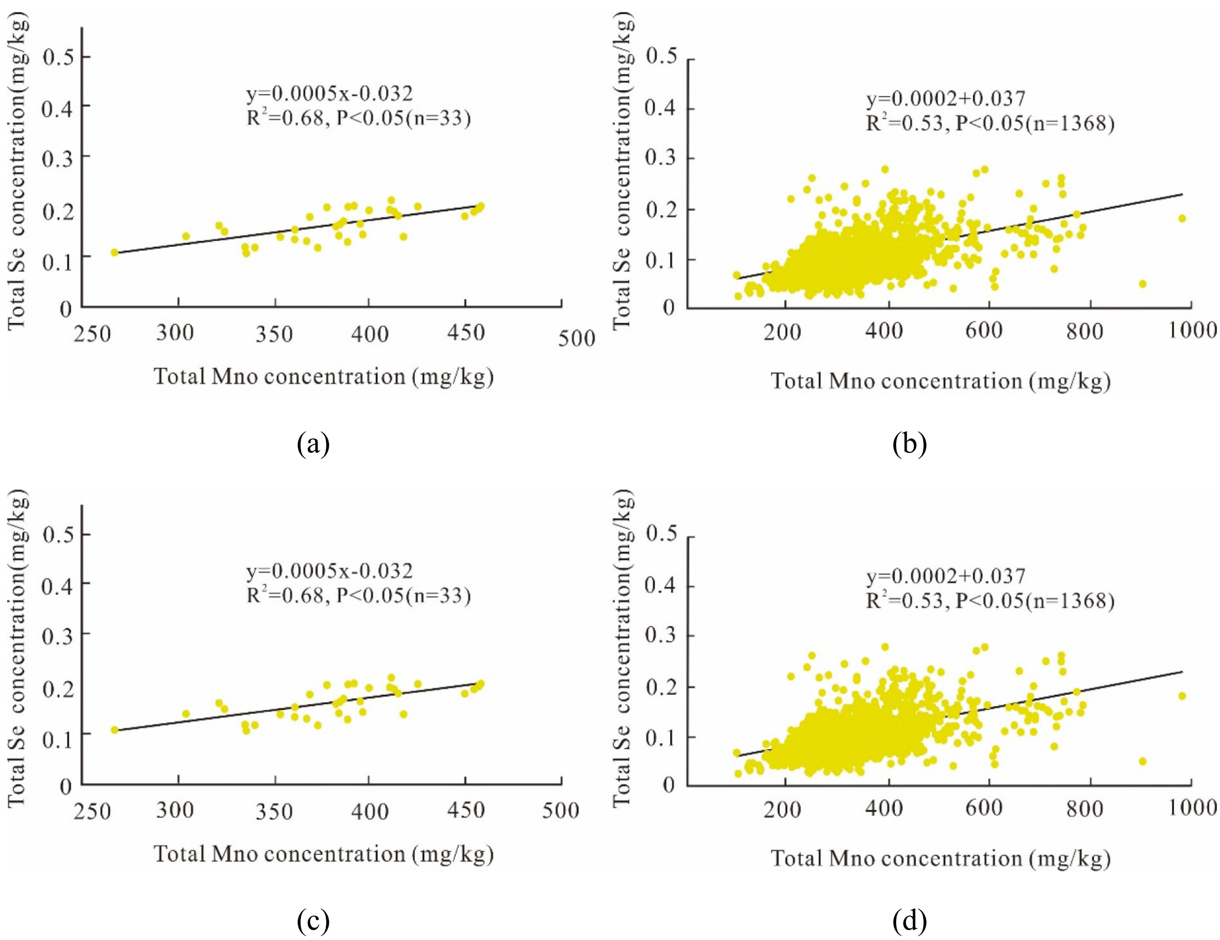

Fig. 6. Correlation between MnO and Se concentrations in different types of soil: (a) chestnut soil, (b) aeolian sandy soil, (c) saline-alkali soil, and (d) alluvial soil.

available K, and the CEC, which exerted an adverse effect on A-Zn and A-B (Fig. S3). It is well known that Se is chemically similar to S, and that Se (VI) enters plants via sulfate transporters (Cherian et al., 2012; Golob et al., 2016; Terry et al., 2000). As shown in Fig. 4, although the ratio of the HA-Se concentration to total-Se increased with decreases in the pH, the same trend was not observed with variations of TOC, which is in contrast to some previous studies (Dinh et al., 2019; Sharma et al., 2015). Moreover, OM exhibits dual effects on Se accumulation and availability due to the presence of different molecular weight organic acids in the soil (Dinh et al., 2018, 2019).

The application of S is not conducive to the absorption of Se by plants (Harris et al., 2014; Hopper and Parker, 1999). Thus, the application of S fertilizer for the regulation of bioavailability and biofortification of Se should take into consideration the following factors: Se species in soils, application management, and soil environmental factors. The positive correlation between A-K and A-B in PC1 indicates that A-K and A-B have an effect on the Se content of crops by promoting the development of plant roots and increasing crop biomass. After the field study, it was found that locally mixed fertilizer is predominantly used to increase the productivity of farmland with a long history of agricultural reclamation. Further, more plant root secretions are released into the soil, which can change the amount of organic acid and regulate the pH of the rhizosphere by increasing or decreasing the secretion of H^+ to inhibit the absorption of heavy metals by plant roots from the soil (Li et al., 2016). Furthermore, root exudates, such as organic acids and amino acids, are utilized by vegetation root microorganisms to decrease the redox potential of root soil compared with non-root soil, thereby reducing valence heavy metals in rhizosphere soil (Dinh et al., 2019). Some secretions may also chelate with heavy metals, including Se, to form insoluble substances. Se is less bioavailable under reducing acid conditions and more mobile and available under oxidizing conditions (Dinh et al., 2019), indicating that fertilizer application indirectly reduced the available Se content in soil during agricultural activities on the southern Songnen Plain (Fig. 8a). PC2 reflects the antipathic relationship of chelation between essential mineral nutrient elements and trace elements of plants in Gannan soil. This is a rather significant result in that there is a negative correlation between active mineral nutrient elements (A-P, A-B, A-K, NH_4^+) and trace elements (A-Fe, A-Cu, A-Mo, A-Zn). The root is the main organ for the plant to absorb trace elements. There was a negative correlation between A-P and A-Zn on PC2. The occurrence of P and Zn in soil can be divided into two stages. Application of P can improve the availability of soil Zn and the two have a synergistic effect. However, the application of high levels of P reduced the availability of soil Zn, and these elements showed an antagonistic effect. Furthermore, studies have found that within the normal range of P application, the absorption of Zn in soil decreased first and then increased, and at a higher P level in soil, the desorption of Zn increased first and then decreased (Zhang et al., 2017, 2012). It is suggested that high levels of residual P from fertilizers in soil may lead to the decline of Zn bioavailability. Moreover, anthropogenic increases of fixation and mobilization of N fertilization promoted the formation of NH_4-N (Frink et al., 1999), which can drive soil acidification (Dinh et al., 2019) and even decrease Se bioavailability via the formation of less available ferric-iron selenite complexes (Gupta et al., 2014). It is also for this reason that A-Fe and Se were negatively correlated with NH^{4+} in PC1 and PC2. Excessive K in the soil first causes the concentration barrier, which makes plants prone to diseases and insect pests, and then antagonizes cationic micronutrients such as Ca, Mo, and Cu in the tillage layer and plant

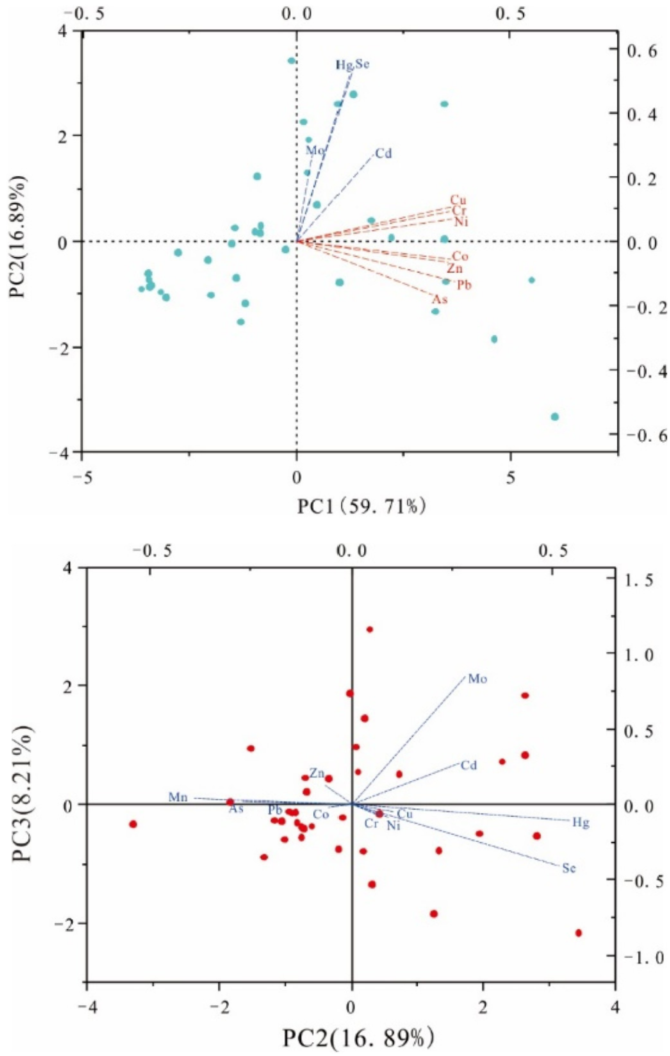

Fig. 7. Loading plots of first three principal components for total Se, Hg, Mo, Mn, Co, As, Cd, Cr, Cu, Pb, and Zn in surface soil of southern Songnen Plain.

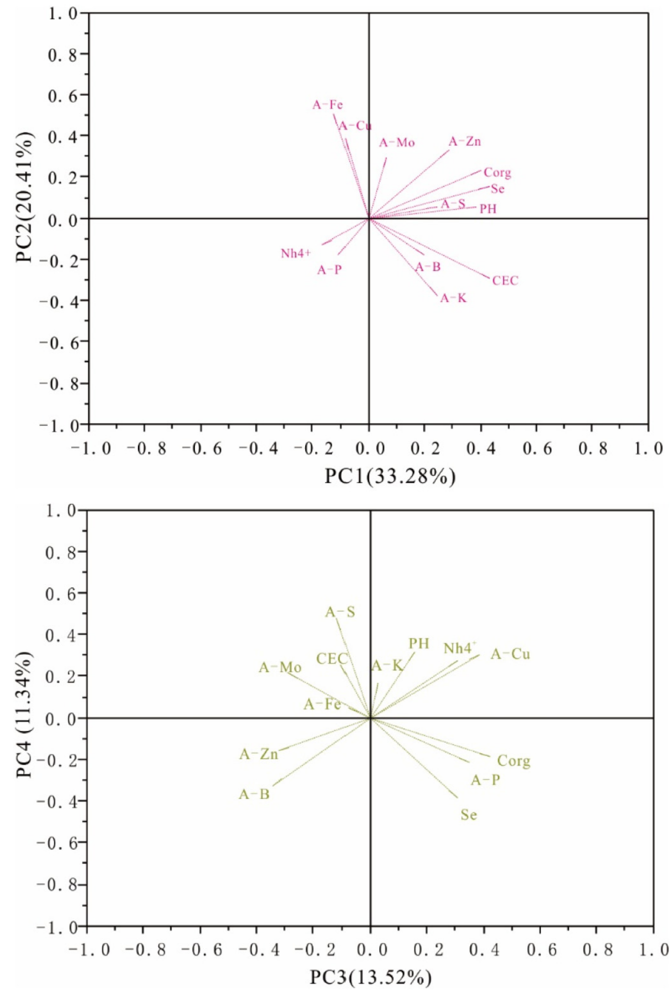

Fig. 8. Loading plots of first four principal components for Se, pH, organic matter (OM), available Fe (A-Fe), available Mo (A-Mo), total K (T-K), Olsen P (A-P), available K (A-K), available Cu (A-Cu), available B (A-B), available Zn (A-Zn), available B (A-B), ammonium ion ($NH4^+$), cation exchange capacity (CEC), organic carbon (Corg) and clay in surface soil of southern Songnen Plain.

(Haynes and Naidu, 1998). Taken together, these results suggested that not only were there an antipathic association between soil Se and nutrient elements, but also reflected overfertilization of soil in China's major grain-producing areas.

Compared with other components, PC3 comprised some interrelated properties, such as A-B, Olsen or extractable P (A-P), Se, and pH (Fig. 8b). This was similar to PC1 and suggests that increasing A-P favored Se desorption from associated or adsorbed fractions and improved A-Se in soil, which was consistent across various soil types on the southern Songnen Plain (Fig. 8). The type of fertilizer applied to crops was also shown to have an important effect (Borowska et al., 2013), whereby the application of P decreased plant Se concentrations (Mora et al., 2008; Hopper and Parker, 1999; Lee et al., 2011). The antagonistic relationship between micronutrients and macro-nutrients was also reflected in PC3.

Surface soil Se concentrations are correlated with Corg, pH, plant net primary productivity (NPP), Fe/Mn/Al concentration, concentration of elements required for plant growth, NSE, precipitation, and surface temperature (Bitterli et al., 2010; Jones et al., 2017). These factors were categorized into four groups ($n = 2052$): climate factors (e.g., NSE, precipitation, and surface temperature), heavy metals (Fe/Mn/Al concentrations), fertilizer elements (N/P/K/S concentrations), and soil properties (pH, NPP, and Corg). According to the path analysis results of structural equation modeling, the concentration of elements that comprise the main ingredients of fertilizer also plays an important role in shaping the spatial distribution of Se in the surface soil, as was observed for Fe/Mn/Al in Gannan County (Sun et al., 2013).

This comprehensive analysis indicated a significant correlation between A-P and Se in soil, in contrast to other elements required for plant growth. Therefore, avoiding overapplication of P in agricultural production is essential for achieving a balance between yield and plant Se concentration, especially in the case of Se (IV) application. Because of residues from long-term applications, the negative relationship between fertilization and the effective expression of Se in crops is likely to become highly complex when different types of fertilizers are applied to different types of arable land (González-Morales et al., 2017; Harris et al., 2014). Thus, the decline in soil fertility in recent years (National Bureau of Statistics of China, 2010; Pan, 2019; Yin, 2019) may prompt farmers in Northeast China to freely use fertilizers to increase crop outputs in agricultural production; however, excessive fertilizer use can greatly influence the efficiency of translocation, uptake, and accumulation of Se in many crop species. Thus, the low-Se content in the soil of the studied area may not be the primary cause of the Se deficiency in the crops.

Factors contributing to the spatial variation of soil Se according to the structural equation modeling path network are shown in Fig. 9. The direct effect of soil properties was 0.47, which was larger than that of heavy metals (0.23). The variations of soil properties and heavy

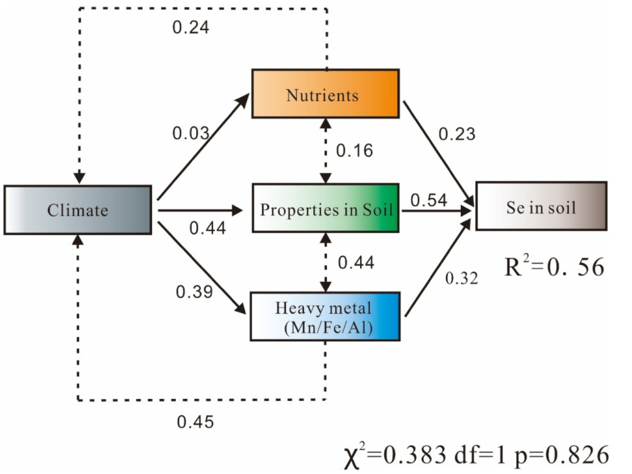

Fig. 9. Structural equation modeling of the spatial distribution of surface soil Se concentration. Solid arrows and corresponding numbers indicate direct effects and the standardized path coefficient (β). β represents the direct effect of one variable on another (maximum 1.0). Dotted arrows and corresponding numbers represent feedbacks and the strength of the feedback effect (maximum 1.0). Double-headed arrows and corresponding numbers indicate collineation between nutrients, soil properties, and heavy metals, and the strength of the collineation (maximum 1.0). All data were logarithmically transformed to conform to a normal distribution in the model. Climate is the PCA1 component of mean annual precipitation, mean annual temperature, and near surface evaporation (S1). The heavy metal factor is the PCA1 component of Se in soil species (S1). Nutrients are the PCA1 component of N/P/K/S fertilizer consumption (S1).

metals are affected by the climate factor (direct effect of 0.24 and 0.35, respectively). For example, precipitation can result in a high Se input from the atmosphere (Blazina et al., 2014). Fe, Mn, and Al are regarded as the major factors for the adsorption process because of their extensive chelating abilities and large specific surface areas (Muller et al., 2012), indicating that Fe/Al oxides affected Se (IV) adsorption and reduced Se bioavailability in 18 types of Chinese soils. This results in the retention of more Se by soil and the absorption of less Se by vegetation (Dinh et al., 2019; Li et al., 2015). Furthermore, the lack of Se migration between Gannan soils and crops (Fig. S3) also confirmed that Se in the surrounding soil did not migrate as much as that in the plant rhizosphere soil.

In contrast, the factors related to plant growth not only have a negative path coefficient with Se but also have a low correlation with climate (0.03), indicating that the nutrient elements in Gannan County are predominantly derived from the addition of artificial fertilizers during agricultural production. According to the agricultural yearbook of Heilongjiang province, the use of agricultural fertilizers, which mainly consist of N, P, and K in the southern part of the Songnen Plain, increased at an annual rate of approximately 2% from 2000 to 2010, reaching 118,567 tons in 2010, predominantly in Northeast China (Administration, 1999). It suggests that excessive use of fertilizers in fields can make it more difficult for soil Se to be absorbed by crops. In addition, as nutrients and heavy metals can result in feedbacks on soil properties, such as those in Fig. 9, interactions among these parameters are likely under future land planning. Thus, the Se content of local agricultural products should be improved in order to ameliorate Se deficiency in local residents caused by insufficient dietary intake.

3.5. Risk assessment of Se in the southern Songnen Plain

The Songnen Plain is one of the first areas to be identified as having Se deficiency related diseases in China. The PDI of Se for residents of the southern Songnen Plain was calculated based on the data of Chen et al. (2011) and using corn kernel samples collected in the present study. The daily Se intake of the majority of the sample population in Heilongjiang province located in the southern part of the Songnen Plain was

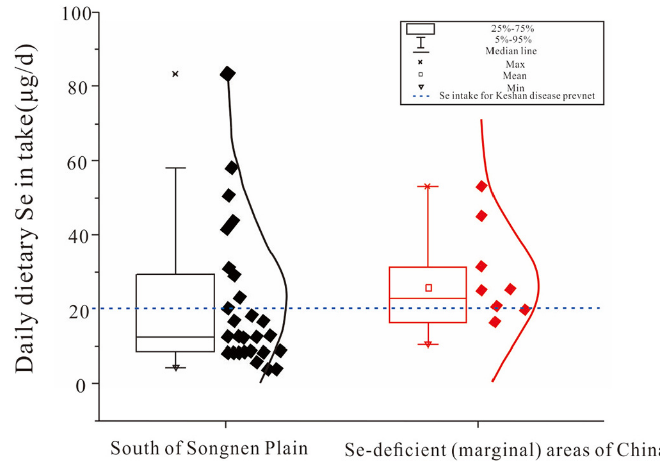

Fig. 10. Daily dietary Se intake in different parts of Songnen Plain and Se-deficient (marginal) areas of China (Dinh et al., 2018).

insufficient, with intakes below those required for KD disease prevention among some residents (Fig. 10; Table S4). The Se nutrition status of half of the population in this area is deficient or sub-deficient; therefore, corrective measures are urgently required, despite the fact that most parts of the study area have normal, marginal, or sufficient Se contents in the soil. Based on previous resident hair sample data, which correspond to dietary intake (Fig. 8), we conclude that Se deficiencies may be less severe in the local population than is suggested by the daily intake data; however, a substantial risk remains.

Interestingly, from the results of the PDI model based on Se intake of staple food (Fig. S4), the high-risk areas with insufficient Se intake were mainly located at the edge of the study area, away from the central cities of the region, while the samples of PDI > 50 were all from around the prefecture-level cities and their surrounding areas. This is probably because people in large towns have more abundant food sources and a smaller proportion of local food intake, which mitigates the effect of low Se levels present in a single-grain food source. However, in areas far away from large cities, the food source of the residents is usually a single source, and hence, the PDI index is significantly lower than in the surrounding areas. Therefore, the gaps in health and safety awareness and food supply in the market cause the low PDI index. The residents in remote areas usually obtain food from a single source; in most cases, the food is produced by themselves or locally, making them vulnerable. Contrarily, the residents in prefecture-level cities and surrounding areas can obtain more exogenous food through a relatively sound commodity supply system in the market, which is likely to reduce the potential human Se deficiency problem. Therefore, in the absence of an immediate increase in Se levels in local crops, Se supplements should be artificially added to the daily diets of the local populations in areas with high incidence of Se-related diseases.

4. Conclusions

A comprehensive analysis of soil samples collected from the southern Songnen Plain revealed that, after decades of artificial addition and disturbance, the surface soil Se content has reached a sufficient level of 0.204 mg/kg; however, crops produced in the region still have a Se-deficient status leading to a risk of endemic diseases in the population of this region. Analysis of the relationship between soil properties and different forms of Se indicates that the bioavailability of Se in the soil is low in the Songnen region. Further statistical analysis of the soil in typical areas and the Se content of crops proved that nutrients (e.g., N, P, K, and S) added as chemical fertilizers impede the soil-to-plant migration of Se in the adjacent soil rhizosphere.

Although the climatic conditions in the Gannan region facilitate the migration of soil Se into plants, extensive fertilizer use to enhance crop growth (which is often neglected in China's agricultural production) has led to low Se contents in agricultural products due to reduced Se absorption. Moreover, despite substantial improvements in soil Se contents in recent decades, future attempts to improve plant productivity may induce Se deficiency in areas that are currently close to becoming Se deficient. This study also confirmed that a decrease in the complexes of Se with other heavy metals (such as Hg and As), originally present in the human body, resulted in an increased bioavailability of heavy metals, thus causing a greater risk of heavy metal poisoning. Therefore, in areas of Se deficiency, like the southern Songnen Plain, the bioavailability of Se levels in plants should be taken into account to prevent underestimating the potential risk of Se deficiency induced by applying conventional fertilizers. Furthermore, the residents of the southern Songnen Plain area remain at a risk of Se deficiency, and hence, the local governments need to develop health risk prevention strategies and mitigate the excessive use of chemical fertilizers. We found that, in terms of Se deficiency, the risks faced by the local residents in the potential risk areas is not uniform. The risk of Se deficiency is mainly due to the dependence of the population in rural areas on a local and low-Se food diet structure. Therefore, the government should specify relevant prevention and control measures for such areas and formulate daily dietary supplements for the residents to effectively control the incidence of Se deficiency related diseases.

CRediT authorship contribution statement

Chenmeng Yang: Data curation, Writing – original draft, Visualization, Investigation, Software, Validation. **Heng Yao:** Supervision, Writing – review & editing. **Yunjie Wu:** Data curation, Writing – original draft, Visualization, Investigation. **Guangyi Sun:** Conceptualization, Methodology, Software, Data curation, Writing – original draft, Supervision, Writing – review & editing. **Wen Yang:** Visualization, Investigation. **Zhonggen Li:** Visualization, Investigation. **Lihai Shang:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.144103.

References

Administration, C.S.F., 1999. Forestry Industry Standard of the People's Republic of China (LY/T 1210 1275-1999) Forest Soil Analysis Method (in Chinese). China Standards Press, Beijing, pp. 321–344.

Ahmad, M., Lee, S.S., Lee, S.E., Al-Wabel, M.I., Tsang, D.C.W., Ok, Y.S., 2017. Biochar-induced changes in soil properties affected immobilization/mobilization of metals/metalloids in contaminated soils. J. Soils Sediments 17 (3), 717–730. https://doi.org/10.1007/s11368-015-1339-4.

Aleksandrovskaia, E., Sindireva, A., Ieronova, V., 2020. Ecological assessment of the action of selenium in a soil-plant system in the conditions of Western Siberia. Bull. Nizhnevartovsk State Univ. (1), 104–110 https://doi.org/10.36906/2311-4444/20-1/16.

Alloway, B.J., 1995. The Origins of Heavy Metals in Soils. Second ed. Springer, Netherlands.

Amaral, A.F.S., Arruda, M., Cabral, S., Rodrigues, A.S., 2008. Essential and non-essential trace metals in scalp hair of men chronically exposed to volcanogenic metals in the Azores, Portugal. Environ. Int. 34 (8), 1104–1108. https://doi.org/10.1016/j.envint.2008.03.013.

Antoniadis, V., Levizou, E., Shaheen, S.M., Ok, Y.S., Sebastian, A., Baum, C., Prasad, M.N.V., Wenzel, W.W., Rinklebe, J., 2017. Trace elements in the soil-plant interface: Phytoavailability, translocation, and phytoremediation–a review. Earth-Sci. Rev. 171, 621–645. https://doi.org/10.1016/j.earscirev.2017.06.005.

Bailey, R.T., 2016. Review: selenium contamination, fate, and reactive transport in groundwater in relation to human health. Hydrogeol. J. 25, 1191–1217. https://doi.org/10.1007/s10040-016-1506-8.

Barron, E., Migeot, V., Séby, F., Ingrand, I., Potin-Gautier, M., Legube, B., Rabouan, S., 2012. Selenium exposure in subjects living in areas with high selenium concentrated drinking water: results of a French integrated exposure assessment survey. Environ. Int. 40, 155–161. https://doi.org/10.1016/j.envint.2011.07.007.

Bitterli, C., Bañuelos, G.S., Schulin, R., 2010. Use of transfer factors to characterize uptake of selenium by plants. J. Geochem. Explor. 107 (2), 206–216. https://doi.org/10.1016/j.gexplo.2010.09.009.

Blazina, T., Sun, Y., Voegelin, A., Lenz, M., Berg, M., Winkel, L., 2014. Terrestrial selenium distribution in China is potentially linked to monsoonal climate. Nat. Commun. 5, 4717. https://doi.org/10.1038/ncomms5717.

Borella, P., Bargellini, A., Incerti Medici, C., 1996. Chemical form of selenium greatly affects metal uptake and responses by cultured human lymphocytes. Biol. Trace Elem. Res. 51, 43–54. https://doi.org/10.1007/BF02790146.

Borowska, K., Grabowska, M., Kozik, K., 2013. Selenium content and enzymatic activity of soil after applying farmyard manure and mineral nitrogen/Zawartość selenu i aktywność enzymatyczna gleby po zastosowaniu nawożenia obornikiem i azotem mineralnym. Environ. Protect. Nat. Resour. Ochrona Środowiska Zasobów Naturalnych 24 (2), 5–10. https://doi.org/10.2478/oszn-2013-0023.

Boyle, D.R., 1981. The analysis of fluorine in geochemical exploration. J. Geochem. Explor. 14, 175–197. https://doi.org/10.1016/0375-6742(81)90111-4.

Cabrerizo, A., Bulteel, D., Waligora, J., Landrot, G., Fonda, E., Olard, F., 2020. Chemical, mineralogical, and environmental characterization of tunnel boring muds for their valorization in road construction: a focus on molybdenum characterization. Environ. Sci. Pollut. Res. https://doi.org/10.1007/s11356-020-09969-6.

Chang, C., Yin, R., Zhang, H., Yao, L., 2019. Bioaccumulation and health risk assessment of heavy metals in the soil–rice system in a typical seleniferous area in Central China. Environ. Toxicol. Chem. 38 (7), 1577–1584. https://doi.org/10.1002/etc.4443.

Chen, J.-S., 2012. An original discovery: selenium deficiency and Keshan disease (an endemic heart disease). Asia Pac. J. Clin. Nutr. 21 (3), 320–326.

Chen, Y., Xu, X., Gao, Q., 2011. The selenium daily intake of the residents in the Southern Songnen Plain of Heilongjiang Province (in Chinese). J. China West Norm. Univ. (Nat. Sci.) 32 (02), 198–200.

Cherian, S., Weyens, N., Lindberg, S., Vangronsveld, J., 2012. Phytoremediation of trace element–contaminated environments and the potential of endophytic bacteria for improving this process. Crit. Rev. Environ. Sci. Technol. 42 (21), 2215–2260. https://doi.org/10.1080/10643389.2011.574106.

Clark, L.C., Combs, G.F., Turnbull, B.W., Slate, E.H., Chalker, D.K., Chow, J., Davis, L.S., Glover, R.A., Graham, G.F., Gross, E.G., Krongrad, A., Lesher, J.L., Park, H.K., Sanders, B.B., Smith, C.L., Taylor, J.R., 1996. Effects of selenium supplementation for cancer prevention in patients with carcinoma of the skin a randomized controlled trial - a randomized controlled trial. Jama 276 (24), 1957–1963. https://doi.org/10.1001/jama.1996.03540240035027.

Coppin, F., Chabroullet, C., Martin-Garin, A., Balesdent, J., Gaudet, J.P., 2006. Methodological approach to assess the effect of soil ageing on selenium behaviour: first results concerning mobility and solid fractionation of selenium. Biol. Fertil. Soils 42 (5), 379–386. https://doi.org/10.1007/s00374-006-0080-y.

Dinh, Q.T., Li, Z., Tran, T.A.T., Wang, D., Liang, D., 2017. Role of organic acids on the bioavailability of selenium in soil: a review. Chemosphere 184, 618–635. https://doi.org/10.1016/j.chemosphere.2017.06.034.

Dinh, Q.T., Cui, Z., Huang, J., Tran, T.A.T., Wang, D., Yang, W., Zhou, F., Wang, M., Yu, D., Liang, D., 2018. Selenium distribution in the Chinese environment and its relationship with human health: a review. Environ. Int. 112, 294–309. https://doi.org/10.1016/j.envint.2017.12.035.

Dinh, Q.T., Wang, M., Tran, T.A.T., Zhou, F., Wang, D., Zhai, H., Peng, Q., Xue, M., Du, Z., Bañuelos, G.S., Lin, Z.-Q., Liang, D., 2019. Bioavailability of selenium in soil-plant system and a regulatory approach. Crit. Rev. Environ. Sci. Technol. 49 (6), 443–517. https://doi.org/10.1080/10643389.2018.1550987.

Fakour, H., Lin, T.-F., Lo, S.-L., 2016. Equilibrium modeling of arsenic adsorption in a ternary arsenic–iron oxide–natural organic matter system. Clean (Weinh) 44, 1287–1295. https://doi.org/10.1002/clen.201500962.

Fang, W., Wu, P., Hu, R., Huang, Z., 2003. Environmental Se-Mo-B deficiency and its possible effects on crops and Keshan-beck disease (KBD) in the Chousang area, Yao County, Shaanxi Province, China. Environ. Geochem. Health 25 (2), 267–280. https://doi.org/10.1023/A:1023271403310.

Feng, P.Y., Zhe, L., Zhe, Y.Y., Huang, J., Liang, D., 2016. Selenate adsorption and desorption in 18 kinds of Chinese soil with their physicochemical properties (in Chinese). Huan Jing Ke Xue 37, 3160–3168.

Fordyce, F.M., 2005. Selenium deficiency and toxicity in the environment. In: Selinus, O., Alloway, B., Centeno, J.A., Finkleman, R.B., Fuge, R., Lindh, U., Smedley, P. (Eds.), Essentials of Medical Geology: Impacts of the Natural Environment on Public Health. Elsevier, Burlington, MA, pp. 373–415.

Fordyce, F.M., 2013. Selenium deficiency and toxicity in the environment. In: Selinus, O. (Ed.), Essentials of Medical Geology, Revised edition Springer Netherlands, Dordrecht, pp. 375–416.

Fordyce, F.M., Zhang, G., Green, K., Liu, X., 2000. Soil, grain and water chemistry in relation to human selenium-responsive diseases in Enshi District, China. Appl. Geochem. 15 (1), 117–132. https://doi.org/10.1016/S0883-2927(99)00035-9.

Fordyce, F., Brereton, N., Hughes, J., Reay, G., Thomas, L., Walker, A., Luo, W., Lewis, J., 2009. The Selenium Content of Scottish Soil and Food Products. Food Standards Agency, Scotland 116 pp. (S14042). (Unpublished).

Frink, C.R., Waggoner, P., Ausubel, J.H., 1999. Nitrogen fertilizer: retrospect and prospect. Proc. Natl. Acad. Sci. U. S. A. 96 (4), 1175–1180. https://doi.org/10.1073/pnas.96.4.1175.

Fu, Q., Wang, D., Li, Y., Yang, X., Yang, Y., 2014. Pedogeochemical research on Se in black soil areas of central Jilin Province (in Chinese). Glob. Geol. 33, 687–694.

Gao, J., Liu, Y., Huang, Y., Lin, Z.-Q., Bañuelos, G.S., Lam, M.H.-W., Yin, X., 2011. Daily selenium intake in a moderate selenium deficiency area of Suzhou, China. Food Chem. 126 (3), 1088–1093. https://doi.org/10.1016/j.foodchem.2010.11.137.

Garcia, M.R., Burdock, R., Cruz, D.Á.M., Crawford, J.W., 2013. Managing the selenium content in soils in semiarid environments through the recycling of organic matter. Appl. Environ. Soil. Sci. 2013. https://doi.org/10.1155/2013/283468 283468, 1 Pp. 10.

Golob, A., Gadžo, D., Stibilj, V., Djikić, M., Gavrić, T., Kreft, I., Germ, M., 2016. Sulphur interferes with selenium accumulation in Tartary buckwheat plants. Plant Physiol. Biochem. 108, 32–36. https://doi.org/10.1016/j.plaphy.2016.07.001.

González-Morales, S., Pérez-Labrada, F., García-Enciso, E., Leija-Martínez, P., Medrano, J., Dávila-Rangel, I., Juárez Maldonado, A., Rivas, E., Benavides-Mendoza, A., 2017. Selenium and sulfur to produce allium functional crops. Molecules 22 (4), 558. https://doi.org/10.3390/molecules22040558.

Gupta, D.K., Chatterjee, S., Datta, S., Veer, V., Walther, C., 2014. Role of phosphate fertilizers in heavy metal uptake and detoxification of toxic metals. Chemosphere 108, 134–144. https://doi.org/10.1016/j.chemosphere.2014.01.030.

Ham, Y.-S., Tamiya, S., 2006. Selenium behavior in open bulk precipitation, soil solution and groundwater in alluvial fan area in Tsukui, Central Japan. Water Air Soil Pollut. 177, 45–57. https://doi.org/10.1007/s11270-005-9062-1.

Hao, Z., Li, Y.H., Liu, Y., Li, H.R., Wang, W.Y., Yu, J.P., 2016. Hair elements and healthy aging: a cross-sectional study in Hainan Island, China. Environ. Geochem. Health 38 (3), 723–735. https://doi.org/10.1007/s10653-015-9755-3.

Harris, J., Schneberg, K.A., Pilon-Smits, E.A.H., 2014. Sulfur–selenium–molybdenum interactions distinguish selenium hyperaccumulator *Stanleya pinnata* from non-hyperaccumulator *Brassica juncea* (Brassicaceae). Planta 239 (2), 479–491. https://doi.org/10.1007/s00425-013-1996-8.

Hartikainen, H., 2005. Biogeochemistry of selenium and its impact on food chain quality and human health. J. Trace Elem. Med. Biol. 18 (4), 309–318. https://doi.org/10.1016/j.jtemb.2005.02.009.

Haynes, R.J., Naidu, R., 1998. Influence of lime, fertilizer and manure applications on soil organic matter content and soil physical conditions: a review. Nutr. Cycl. Agroecosyst. 51 (2), 123–137. https://doi.org/10.1023/A:1009738307837.

He, J.-H., Zheng, Z., 2008. Investigation and evaluation of selenium nutrition in Huaibei inhabitants (in Chinese). J. Environ. Health 025 (5), 426–428.

Hinsinger, P., 2001. Bioavailability of soil inorganic P in the rhizosphere as affected by root-induced chemical changes: a review. Plant Soil 237 (2), 173–195. https://doi.org/10.1023/A:1013351617532.

Hönicke, P., Kayser, Y., Beckhoff, B., Müller, M., Dousse, J.-C., Hoszowska, J., Nowak, S.H., 2012. Characterization of ultra-shallow aluminum implants in silicon by grazing incidence and grazing emission X-ray fluorescence spectroscopy. J. Anal. At. Spectrom. 27, 1432–1438. https://doi.org/10.1039/C2JA10385K.

Hopper, J.L., Parker, D.R., 1999. Plant availability of selenite and selenate as influenced by the competing ions phosphate and sulfate. Plant Soil 210 (2), 199–207. https://doi.org/10.1023/A:1004639906245.

Hou, Q., Yang, Z., Ji, J., Tao, Y., Yuan, X.J., 2014. Annual net input fluxes of heavy metals of the agro-ecosystem in the Yangtze River delta, China. J. Geochem. Explor. 139 (1), 68–84. https://doi.org/10.1016/j.gexplo.2013.08.007.

Huang, B.F., Xin, J.L., Dai, H.W., Zhou, W.J., 2017. Effects of interaction between cadmium (Cd) and selenium (Se) on grain yield and Cd and Se accumulation in a hybrid rice (*Oryza sativa*) system. J. Agric. Food Chem. 65 (43), 9537–9546. https://doi.org/10.1021/acs.jafc.7b03316.

Jia, M., Zhang, Y., Huang, B., Zhang, H., 2018. Source apportionment of selenium and influence factors on its bioavailability in intensively managed greenhouse soil: a case study in the east bank of the Dianchi Lake, China. Ecotoxicol. Environ. Saf. 170, 238–245. https://doi.org/10.1016/j.ecoenv.2018.11.133.

Jones, G., Droz, B., Greve, P., Gottschalk, P., Poffet, D., McGrath, S., Seneviratne, S., Smith, P., Winkel, L., 2017. Selenium deficiency risk predicted to increase under future climate change. Proc. Natl. Acad. Sci. U. S. A. 114, 2848–2853. https://doi.org/10.1073/pnas.1611576114.

Kamei-Ishikawa, N., Tagami, K., Uchida, S., 2007. Sorption kinetics of selenium on humic acid. J. Radioanal. Nucl. Chem. 274 (3), 555–561. https://doi.org/10.1007/s10967-006-6951-8.

Khan, M.A.K., Wang, F., 2009. Mercury-selenium compounds and their toxicological significance: toward a molecular understanding of the mercury-selenium antagonism. Environ. Toxicol. Chem. 28 (8), 1567–1577. https://doi.org/10.1897/08-375.1.

Lee, S., Woodard, H., Doolittle, J., 2011. Effect of phosphate and sulfate fertilizers on selenium uptake by wheat (*Triticum aestivum*). Soil Sci. Plant Nutr. 57, 696–704. https://doi.org/10.1080/00380768.2011.623282.

Li .L.Z., G.H., 2017. Investigation and Study on Soil Environment in Typical Cities of "Two Great Plains" Comprehensive Reform Pilot Area in Heilongjiang Province. Heilongjiang People's Publishing House, Harbin (in Chinese).

Li, S., Xiao, T., Zheng, B., 2012. Medical geology of arsenic, selenium and thallium in China. Sci. Total Environ. 421-422, 31–40. https://doi.org/10.1016/j.scitotenv.2011.02.040.

Li, Z., Man, N., Wang, S.S., Liang, D.L., Liu, J.J., 2015. Selenite adsorption and desorption in main Chinese soils with their characteristics and physicochemical properties. J. Soils Sediments 15 (5), 1150–1158. https://doi.org/10.1007/s11368-015-1085-7.

Li, J., Peng, Q., Liang, D., Liang, S., Chen, J., Sun, H., Li, S., Lei, P., 2016. Effects of aging on the fraction distribution and bioavailability of selenium in three different soils. Chemosphere 144, 2351–2359. https://doi.org/10.1016/j.chemosphere.2015.11.011.

Lin, H.L., Zhu, R.L., Yu, L., Cheng, Y.X., Zhu, R.R., Liu, P., Ren, Z.H., 2020. Determination of arsenic, mercury, selenium, antimony and bismuth in soil and sediments by water bath digestion-atomic fluorescence spectrometry. Spectrosc. Spectral Anal. 5, 1528–1533 (in Chinese).

Mader, P., Fliessbach, A., Dubois, D., Gunst, L., Fried, P., Niggli, U., 2002. Soil fertility and biodiversity in organic farming. Science 296, 1694–1697. https://doi.org/10.1126/science.1071148.

Mora, M.d.l.L., Pinilla, L., Rosas, A., Cartes, P., 2008. Selenium uptake and its influence on the antioxidative system of white clover as affected by lime and phosphorus fertilization. Plant Soil 303 (1), 139–149. https://doi.org/10.1007/s11104-007-9494-z.

Muller, J., Abdelouas, A., Ribet, S., Grambow, B., 2012. Sorption of selenite in a multi-component system using the "dialysis membrane" method. Appl. Geochem. 27 (12), 2524–2532. https://doi.org/10.1016/j.apgeochem.2012.07.023.

National Bureau of Statistics of China, 2010. Heilongjiang Statistical Yearbook 2013. China Statistics Press, Beijing.

National Bureau of Statistics of China, 2020. China Statistical Yearbook. China Statistics Press, Beijing.

Nicholson, F.A., Smith, S.R., Alloway, B.J., Carlton-Smith, C., Chambers, B.J., 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. Sci. Total Environ. 311 (1), 205–219. https://doi.org/10.1016/S0048-9697(03)00139-6.

Page, A.L., Miller, R.H., Keeney, D.R., 1982. Methods of Soil Analysis: Chemical and Microbiological Properties. second ed. American Soc. of Agronomy (Publ.), Madison, Wisconsin, USA.

Pan, X., 2019. Spatial and Temporal Variations of Fertilizer Usage Across Prefecture-level Cities in China From 2000 to 2015. (Master Thesis). Yunnan University, Yunnan, China.

Panchal, S.K., Wanyonyi, S., Brown, L., 2017. Selenium, vanadium, and chromium as micronutrients to improve metabolic syndrome. Curr. Hypertens. Rep. 19 (3), 10. https://doi.org/10.1007/s11906-017-0701-x.

Peng, Q., Guo, L., Ali, F., Li, J., Qin, S., Feng, P., Liang, D., 2016. Influence of Pak choi plant cultivation on Se distribution, speciation and bioavailability in soil. Plant Soil 403 (1), 331–342. https://doi.org/10.1007/s11104-016-2810-8.

Rayman, M.P., 2000. The importance of selenium to human health. Lancet 356 (9225), 233–241. https://doi.org/10.1016/S0140-6736(00)02490-9.

Shaheen, S.M., Ali, R.A., Abowaly, M.A., Rabie, A.E.-M.A., El Abbasy, N.E., Rinklebe, J., 2018. Assessing the mobilization of As, Cr, Mo, and Se in Egyptian lacustrine and calcareous soils using sequential extraction and biogeochemical microcosm techniques. J. Geochem. Explor. 191, 28–42. https://doi.org/10.1016/j.gexplo.2018.05.003.

Shao, X., Cheng, H., Li, Q., Lin, C., 2013. Anthropogenic atmospheric emissions of cadmium in China. Atmos. Environ. 79, 155–160. https://doi.org/10.1016/j.atmosenv.2013.05.055.

Sharma, V.K., McDonald, T.J., Sohn, M., Anquandah, G.A.K., Pettine, M., Zboril, R., 2015. Biogeochemistry of selenium. A review. Environ. Chem. Lett. 13 (1), 49–58. https://doi.org/10.1007/s10311-014-0487-x.

Shi, Z., Pan, P., Feng, Y., Kan, Z., Li, Z., Wei, F., 2016. Environmental water chemistry and possible correlation with Kaschin-Beck disease (KBD) in northwestern Sichuan, China. Environ. Int. 99, 282–292. https://doi.org/10.1016/j.envint.2016.12.006.

Stasinakis, A.S., Thomaidis, N.S., 2010. Fate and biotransformation of metal and metalloid species in biological wastewater treatment processes. Crit. Rev. Environ. Sci. Technol. 40 (4), 307–364. https://doi.org/10.1080/10643380802339026.

Steinbrenner, H., Sies, H., 2009. Protection against reactive oxygen species by selenoproteins. Biochim. Biophys. Acta 1790 (11), 1478–1485. https://doi.org/10.1016/j.bbagen.2009.02.014.

Sun, G., Chen, Y., Bi, X., Yang, W., Chen, X., Zhang, B., Cui, Y., 2013. Geochemical assessment of agricultural soil: a case study in Songnen-Plain (Northeastern China). CATENA 111, 56–63. https://doi.org/10.1016/j.catena.2013.06.026.

Supriatin, S., Terrones, C., Bussink, W., Weng, L., 2015. Drying effects on selenium and copper in 0.01 M calcium chloride soil extractions. Geoderma 255, 104–114. https://doi.org/10.1016/j.geoderma.2015.04.021.

Supriatin, S., Weng, L., Comans, R.N., 2016. Selenium-rich dissolved organic matter determines selenium uptake in wheat grown on low-selenium arable land soils. Plant Soil 408 (1), 73–94. https://doi.org/10.1007/s11104-016-2900-7.

Tamás, M., 2015. Investigation of Selenium Content of Wheat Cultivated on Various Soil Types Located in Different Regions of Romania. (PhD Thesis). University of Debrecen, Debrecen Hungary (28 pp.).

Tan, J.A., Zhu, W.Y., Wang, W.Y., Li, R.B., Hou, S.F., Wang, D.C., Yang, L.S., 2002. Selenium in soil and endemic diseases in China. Sci. Total Environ. 284 (1), 227–235. https://doi.org/10.1016/S0048-9697(01)00889-0.

Taylor, D., Dalton, C., Hall, A., Woodroofe, M.N., Gardiner, P.H.E., 2009. Recent developments in selenium research. Br. J. Biomed. Sci. 66, 107–116. https://doi.org/10.1080/09674845.2009.11730256.

Terry, N., Zayed, A.M., de Souza, M.P., Tarun, A.S., 2000. Selenium in higher plants [review]. Annu. Rev. Plant Physiol. Plant Mol. Biol. 51 (4), 401–432. https://doi.org/10.1146/annurev.arplant.51.1.401.

Tian, H., Ma, Z., Chen, X., Zhang, H., Bao, Z., Wei, C., Xie, S., Wu, S., 2016. Geochemical characteristics of selenium and its correlation to other elements and minerals in selenium-enriched rocks in Ziyang County, Shaanxi Province, China. J. Earth Sci. 27, 763–776. https://doi.org/10.1007/s12583-016-0700-x.

Wang, Z., Gao, Y., 2001. Biogeochemical cycling of selenium in Chinese environments. Appl. Geochem. 16 (11), 1345–1351. https://doi.org/10.1016/S0883-2927(01)00046-4.

Wang, X.D., Xu, Z.L., Xie, Z.L., Yang, Q.J., 2003. The change of plumbum content in TSP of Changchun ambient air before and after using lead-free gasoline. Acta Sci. Nat. Univ. Jilin. 2003–2004.

Wang, C., Ji, J., Zhu, F., 2017. Characterizing Se transfer in the soil-crop systems under field condition. Plant Soil 415, 535–548. https://doi.org/10.1007/s11104-017-3185-1.

Wang, X., Yuan, W., Lin, C.-J., Zhang, L., Zhang, H., Feng, X., 2019. Climate and vegetation as primary drivers for global mercury storage in surface soil. Environ. Sci. Technol. 53 (18), 10665–10675. https://doi.org/10.1021/acs.est.9b02386.

Xu, Q., Kuang, E., Zhang, J., Wei, D., Su, Q., Han, J., 2016. Distribution of selenium and its infuencing factors in soils of Heilongjiang Province, China. Acta Pedol. Sin. 53, 1262–1274. https://doi.org/10.11766/trxb201511300524.

Xu, Y.F., Li, Y.H., Li, H.R., Wang, L., Liao, X.Y., Wang, J., Kong, C., 2018. Effects of topography and soil properties on soil selenium distribution and bioavailability (phosphate extraction): a case study in Yongjia County, China. Sci. Total Environ. 633, 240–248. https://doi.org/10.1016/j.scitotenv.2018.03.190.

Xueqi, X., Zhongfang, Y., Yuan, X., Yujun, C., Yansheng, L., Qingye, H., Tao, Y., 2012. Geochemical circling of soil Se on the Southern Song-Nen Plain, Heilongjiang Province (in Chinese). Geoscience 26 (5) (16–24+30).

Yang, C.M., Sun, G.Y., Zhang, C., Chen, Y.P., Yang, W., Shang, L.H., 2019. A new geochemical method for determining the sources of atmospheric particles: a case study from Gannan, Northeast China. Atmosphere 10 (10), 632. https://doi.org/10.3390/atmos10100632.

Yao, Y., Pei, F., Kang, P., 2011. Selenium, iodine, and the relation with Kashin-Beck disease. Nutrition 27 (11), 1095–1100.

Yin, N., 2019. Evaluation of Carbon Emission Efficiency of Planting Industry and Its Influencing Factors in Heilongjiang Province (in Chinese). (Master Thesis). Northeast Agricultural University, Harbin, China.

Yiyong, Y., Huaixing, W., Linqing, C., Zhengxuan, W., Liuen, W., of, I.p., Xianling, Z., Liangjian, Z., Runlin, F., Runping, Y., 2002. Effect of selenium Qishen pill on blood lipid and immunoglobulin of Keshan disease patients. Chin. J. Control Endemic Dis. 03, 176–177.

Yuan, L., Yin, X., Zhu, Y., Fei, L., Yang, H., Ying, L., Lin, Z., 2012. Selenium in plants and soils, and selenosis in Enshi, China: implications for selenium biofortification. In: Yin, X., Yuan, L. (Eds.), Phytoremediation and Biofortification. SpringerBriefs in Molecular Science. Springer, Dordrecht https://doi.org/10.1007/978-94-007-1439-7_2.

Zhang, Y.-Q., Deng, Y., Chen, R.-Y., Cui, Z.-L., Chen, X.-P., Yost, R., Zhang, F.-S., Zou, C.-Q., 2012. The reduction in zinc concentration of wheat grain upon increased phosphorus-fertilization and its mitigation by foliar zinc application. Plant Soil 361 (1), 143–152. https://doi.org/10.1007/s11104-012-1238-z.

Zhang, H., Feng, X., Chan, H.M., Larssen, T., 2014. New insights into traditional health risk assessments of mercury exposure: implications of selenium. Environ. Sci. Technol. 48 (2), 1206–1212. https://doi.org/10.1021/es4051082.

Zhang, W., Chen, X.-X., Liu, Y.-M., Liu, D.-Y., Chen, X.-P., Zou, C.-Q., 2017. Zinc uptake by roots and accumulation in maize plants as affected by phosphorus application and arbuscular mycorrhizal colonization. Plant Soil 413 (1), 59–71. https://doi.org/10.1007/s11104-017-3213-1.

Zhu, J., Zuo, W., Liang, X., Li, S., Zheng, B., 2004. Occurrence of native selenium in Yutangba and its environmental implications. Appl. Geochem. 19 (3), 461–467. https://doi.org/10.1016/j.apgeochem.2003.09.001.

Zhu, J.M., Wang, N., Li, S., Li, L., Su, H., Liu, C.X., 2008. Distribution and transport of selenium in Yutangba, China: impact of human activities. Sci. Total Environ. 392 (2–3), 252–261. https://doi.org/10.1016/j.scitotenv.2007.12.019.

Zhuang, P., McBride, M.B., Xia, H., Li, N., Li, Z., 2009. Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. Sci. Total Environ. 407 (5), 1551–1561. https://doi.org/10.1016/j.scitotenv.2008.10.061.