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Influence of Long-Term Fertilization on Selenium Accumulation in Soil and Uptake by Crops

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ABSTRACT

Continuous applications of organic and inorganic fertilizers can affect soil and food quality with respect to selenium (Se) concentrations. A long-term (over 20 years) experimental field study, started in 1989, was conducted to investigate the changes in soil Se fractions and its uptake by crops, as affected by different fertilizer practices, in the North China Plain with an annual crop rotation of winter wheat and summer maize. The long-term experiment was arranged in a complete randomized block design consisting of 4 replications with 7 fertilizer treatments: 1) organic compost (OC), 2) half organic compost plus half N-P-K chemical fertilizers (OC + NPK), 3) N-P-K fertilizers (NPK), 4) N-P fertilizers (NP), 5) P-K fertilizers (PK), 6) N-K fertilizers (NK), and 7) an un-amended control. Soil samples from the surface (20 cm) were collected in 1989, 1994, 1999, 2004 and 2009 to characterize Se and other soil properties. In 2009, the average soil Se concentrations in the treatments (149 ± 8 μg kg^{-1}) were higher than those in the soil samples collected in 1989 at the beginning of the experiment (112 ± 4 μg kg^{-1}), and decreased in the order of OC > OC + NPK > NPK ≈ NP > PK ≈ NK > control. Sequential extraction showed the oxidizable fraction (50.06% ± 3.94%) was the dominant form of Se in the soil, followed by the residual fraction (24.12% ± 2.89%), exchangeable fraction (15.09% ± 4.34%) and Fe-Mn oxides fraction (10.73% ± 4.04%). With an increase of soil K, the exchangeable Se concentrations in the soil increased. The Se concentrations in the soil tillage layer (0–20 cm) were mainly related to soil organic carbon (SOC), although different contributions came from atmospheric deposition, irrigation and fertilizers. With the accumulation of SOC, the uptakes of soil Se by two crops were inhibited. For the OC and OC + NPK treatments, Se concentrations in wheat grains were lower than the critical standard of Se in stable food (100 μg kg^{-1}). Additionally, Se concentrations in grains were also decreased by the deficiencies of major soil nutrients, especially P.

Key Words: agricultural soil, essential nutrient, fertilizer practices, Se deficiency, Se fractions

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INTRODUCTION

Selenium (Se) was confirmed as an essential nutrient to human and animals by the World Health Organization in the 1970s (Combs, 2001; Beljanski, 2007). Se deficiency in soils often results in low Se concentrations in foods and negatively affects human or animal health (Combs, 2001; Tan *et al.*, 2002). Selenium concentrations in staple foods should not be lower than the critical standard of 100 μg kg^{-1}, below which people's basic needs can hardly be met (Combs, 2001; Beljanski, 2007). On the other hand, Se can be harmful to human health if it is present in high concentrations in the ecosystem (Combs, 2001; White and Brown, 2010).

The natural contents of Se in soils are dominated by soil parent materials. With the average concentration of about 200 μg kg^{-1}, Se concentrations in different soils range from 100 to 2 000 μg kg^{-1} (EMS, 1990; Gupta and Gupta, 2000; Wang and Gao, 2001). In China, the average abundance of Se in the earth's crust is only 58 μg kg^{-1}, much lower than that in other parts of the world (EMS, 1990; Wang and Gao, 2001). An extensive low belt of Se stretches from Heilongjiang Province in the Northeast to Yunnan Province in the Southwest (Wang and Gao, 2001). Addition of Se to soils in this area would be beneficial.

In an agricultural system, soil Se is mined through crop uptake which is compensated by the application of Se-containing fertilizer (Blagojevic *et al.*, 1998; Edelbauer and Eder, 2001; Yu *et al.*, 2011). The contribution of fertilizer applications to soil Se is a function of Se contents in fertilizers and application rates. The ap-

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plication of phosphate fertilizer or sewage sludge containing Se resulted in a significant accumulation of Se in some agricultural soils (Blagojevic *et al.*, 1998; Edelbauer and Eder, 2001; Eurola *et al.*, 2004). Se accumulation in soils is also attributed to atmospheric deposition, irrigation water, and other industrial sources (Cheng, 2003; Wen and Carignan, 2007; Ali-Khodja *et al.*, 2008; Dhillon and Dhillon, 2009).

The solubility, mobility and bioavailability of Se in the environment depend strongly on its specific chemical forms, and how strongly they are bound to soils. For instance, the dominant form of Se in alkaline soils is selenate, whose adsorption in soils is easily affected by soil competitive ions (Woodbury *et al.*, 1999; Dhillon and Dhillon, 2000). In addition to soil Fe and Mn oxides, Se accumulation in soils is also related to soil organic carbon (SOC) contents due to the chelation of Se by soil organic matter (oxidizable-bound) (Blagojevic *et al.*, 1998; Borowska and Koper, 2010; Shand *et al.*, 2010). Soil Se in the residual fraction is stable in soils and is difficult to extract by some chemical solutions (Martens and Suarez, 1997; Keskinen *et al.*, 2009). Determination of Se fractions, such as "exchangeable" or "oxidizable-bound", can be a good indicator of Se influences on the environment. As a result of this practicality, single and sequential extraction schemes have been developed for the determination of various forms of Se in soils and sediments (Martens and Suarez, 1997; Wu *et al.*, 2004; Keskinen *et al.*, 2009).

Application of different fertilizers not only causes various extents of Se accumulation in soils, but also results in soil Se changes in different fractions and their availabilities to crops. As Se is a trace element in soils, more Se added by different sources can be adsorbed in soils. Se adsorption in soils is not only affected by soil surface charges, but also relates to the competitive ions in soil solution, such as K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, *etc.* (Woodbury *et al.*, 1999; Dhillon and Dhillon, 2000). Affected by different chemical fertilizers, Se adsorptions in soils are often decreased due to the input of competitive ions (Ellis and Salt, 2003; Sors *et al.*, 2005). Selenium adsorption in soils increases through the chelation of Se with soil organic matters if compost is added. However, Se uptake by crops is inhibited by organic matter addition (Dhillon and Dhillon, 1999; Wang and Gao, 2001; Eurola *et al.*, 2004).

The North China Plain (NCP) is one of the most important grain bases in China, and produces about one fourth of the country's total cereal crops. The fertility and productivity of soils in the region not only play important roles in sustaining the local economy, but also in national food security as a whole. Therefore, its agro-ecological safety has attracted great attention lately. With the long-term intensive high-yield crop productions, more pollutants have been accumulated in soils and some have transferred to groundwater and food chains (Zhu *et al.*, 2005; Zhao *et al.*, 2007; Cao and Zhou, 2008; Zheng *et al.*, 2008). This accumulation is probably attributed to fertilizer applications since industry is not prevailing in the NCP. Being located in the low Se belt, most of the soils in the NCP are naturally deficient in Se, which may pose potential health risk to people in the region. However, Se behaviors in soils, such as accumulations and availabilities to crops, are often neglected, since they are usually not the key factors affecting soil fertilities and crop productions (Zhu *et al.*, 2005; Cao and Zhou, 2008; Huang *et al.*, 2011; Zhao *et al.*, 2013). Therefore, it is necessary to explore the factors affecting Se concentrations in soils, and to address the bioavailability of Se species in soils for assessing its impact on food and environmental quality. The objectives of this study were to investigate the rate of Se accumulation in an intensively cultivated agricultural soil of the NCP and the changes in soil Se fractions and its uptake by crops as affected by different fertilizer practices.

MATERIALS AND METHODS

Study area and field experiment

A long-term fertilization experiment was carried out at the Fengqiu Agro-Ecological Experimental Station (114° 24′ E, 35° 00′ N) of Chinese Academy of Sciences in Henan Province, China. The soil was classified as Calcaric Fluvisol according to World Reference Base for Soil Resources (Shi *et al.*, 2010), which is the predominant soil in the region and has a sandy-loam texture. The field had been under the rotation of winter wheat (*Triticum aestivum* L.) and summer maize (*Zea mays* L.) in every year. The winter wheat was grown from October to next May and summer maize from June to September of each year.

The field experiment was initiated in October 1989. Prior to 1989, the field had not received any fertilizer application for 3 years (1987–1989) to remove any residual effects from previous fertilization and obtain a uniform field site. The initial soil contained organic C 5.83 g kg^{-1}, total N 0.45 g kg^{-1}, total P 0.50 g kg^{-1}, total K 18.6 g kg^{-1}, mineral N 9.51 mg kg^{-1}, plant available P 1.93 mg kg^{-1}, plant available K 78.8 mg kg^{-1} and total Se 121 μg kg^{-1}. Soil pH was 8.65. The experiment was installed in a complete randomized block design consisting of 7 fertilizer treatments with 4 replicates. Each plot measured 9.5 m × 5 m and