Environmental Pollution 188 (2014) 27–36

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Understanding the paradox of selenium contamination in mercury mining areas: High soil content and low accumulation in rice

Hua Zhang [a,b], Xinbin Feng [a,*], Chengxin Jiang [c], Qiuhua Li [d], Yi Liu [e], Chunhao Gu [a], Lihai Shang [a], Ping Li [a], Yan Lin [b], Thorjørn Larssen [b]

[a] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 46 Guanshui Road, Guiyang 550002, China
[b] Norwegian Institute for Water Research (NIVA), Gaustadalléen 21, 0349 Oslo, Norway
[c] Academy of Engineering Institute, China University of Geosciences, Wuhan 430074, China
[d] Key Laboratory for Information System of Mountainous Area and Protection of Ecological Environment of Guizhou Province, Guizhou Normal University, Guiyang 550001, China
[e] Guizhou Academy of Geological Survey, Guiyang 55005, China

A R T I C L E I N F O

Article history:
Received 23 October 2013
Received in revised form
10 January 2014
Accepted 14 January 2014

Keywords:
Bioaccumulation
Food consumption
Mercury mining areas
Soil selenium contamination
Sequential partial dissolution

A B S T R A C T

Rice is an important source of Se for billions of people throughout the world. The Wanshan area can be categorized as a seleniferous region due to its high soil Se content, but the Se content in the rice in Wanshan is much lower than that from typical seleniferous regions with an equivalent soil Se level. To investigate why the Se bioaccumulation in Wanshan is low, we measured the soil Se speciation using a sequential partial dissolution technique. The results demonstrated that the bioavailable species only accounted for a small proportion of the total Se in the soils from Wanshan, a much lower quantity than that found in the seleniferous regions. The potential mechanisms may be associated with the existence of Hg contamination, which is likely related to the formation of an inert Hg–Se insoluble precipitate in soils in Wanshan.

1. Introduction

Selenium (Se) is among the most controversial trace elements because it can be both toxic and nutritional. It is toxic at high levels and essential within a physiologically appropriate margin. Se can have adverse effects on human health in excess or deficiency. Se exists in human and animal selenoproteins as selenocysteine and selenomethionine and is incorporated into the active sites of antioxidant selenoenzymes (Rayman, 2012). For many years, glutathione peroxidase was considered the main selenoprotein; however, later discoveries indicated that glutathione peroxidase is only one of at least 25 genetically encoded selenoproteins (including multiple forms of glutathione peroxidases and thioredoxin reductases) (Reeves and Hoffmann, 2009). Through its incorporation into selenoenzymes, Se is involved in important biological functions that affect such processes as free radical metabolism, immune function, reproductive function and apoptosis (Fordyce, 2013; Rayman, 2012). Severe Se deficiencies (e.g., <10 μg/day) are likely involved in the etiology of a well-known cardiomyopathy endemic in China (Keshan disease) (KDRG, 1979). Therefore, adequate Se intake is important to maintain normal physiological function in humans. The safe intake range of Se as recommended by the Chinese Nutrition Society is rather narrow: 50–200 μg/day for adults (identical to that recommended by the U.S. National Research Council) (CNS, 1990; Fordyce, 2013).

The distribution of Se is uneven over the Earth's surface. Seleniferous and Se-deficient geo-ecosystems can be formed within limited geographic zones (Tan et al., 2002). Several areas, such as Enshi in Hubei, China; the Great Plains of the USA and Canada; and portions of Ireland, Colombia and Venezuela are known seleniferous areas. However, on a global basis, areas of low-Se or Se-deficient soil are more common than areas of Se-rich soil. Over 40 countries, including China, Denmark, Finland, New Zealand and Russia (eastern and central Siberia), have been designated as low-Se or Se-deficient according to the World Health Organization (WHO) (Combs, 2001; Li et al., 2007a). Globally, between 0.5 and 1 billion people are estimated to suffer from Se deficiency (Combs, 2001).

On the periodic table, Se belongs to the same group of elements as sulfur. Consequently, its biogeochemical properties are analogous to those of sulfur, one of the most common elements in Earth's

* Corresponding author.
E-mail address: fengxinbin@vip.skleg.cn (X. Feng).

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http://dx.doi.org/10.1016/j.envpol.2014.01.012

crust. Selenium is often found in association with sulfur-containing minerals. In the natural environment, Se typically exists in four different oxidation states (−II, 0, +IV, +VI) as selenide, elemental Se, dissolved selenates (SeO_4^{2-}) and selenites (SeO_3^{2-}); under normal soil conditions, Se exists as insoluble elemental Se (Se^0), selenides (Se^{2-}) and organo-selenium compounds (containing C–Se–C chemical bonds), such as volatile methyl-selenides, trimethyl-selenonium ions and several seleno-amino acids (Bujdoš et al., 2005).

China has abundant Se resources (e.g., Enshi in Hubei province and Ziyang in Shanxi province, where topsoil Se exceeds 1.0 mg kg^{-1}) in some regions and low-Se or Se-deficient soils in others (over two-thirds of the country) (Tan et al., 2002). As shown in Fig. 1, a belt of low-Se soil (the "Se deficiency belt"), primarily composed of brown soil, stretches from the northeast to the southwest across approximately 22 provinces or districts, including Heilongjiang, Jilin, Liaoning, Beijing, Shandong, Inner Mongolia, Gansu, Sichuan, Yunnan, Tibet and Zhejiang (Tan, 1989).

Daily food consumption is typically the primary route for human Se intake. In addition to fish, which is known to accumulate high Se loads, dietary rice is of great significance for maintaining sufficient Se intake for billions of people with a rice-based diet, especially those in Asian countries, including China, where rice is a staple food (Zhang et al., 2012). A recent global survey of rice indicated that approximately 75% of grain samples failed to meet the recommended Se intake quantity for human health (Williams et al., 2009). Although rice grains typically contain much lower Se concentrations than meat and fish (Navarro-Alarcon and Cabrera-Vique, 2008), rice is one of the primary Se sources (40–70%) for rice-eating populations due to their high rice intake (e.g., 300–600 g/day/person) (Williams et al., 2009; Zhang et al., 2012).

Rice can efficiently assimilate inorganic Se into organic forms (Li et al., 2010), which enhances the nutritional efficacy of Se. Organic forms of Se are more bioavailable to humans than inorganic forms are (Rayman et al., 2008). Several studies have revealed that the total Se content in rice is dominated by an organic form, protein-bound selenomethionine, which accounts for more than 80% of the total Se (Fang et al., 2009; Li et al., 2010; Mar et al., 2009).

In addition to serving as a micronutrient, Se can inhibit the harmful effects of Hg exposure, potentially making it the most important micronutrient in rice in regions where rice is the staple food (Khan and Wang, 2009). One good example is a recent study by Li et al. (2012), which indicated that supplementation with organic Se substantially improved Hg excretion in individuals and inhibited the oxidative damage from long-term Hg exposure.

Although usually overlooked by environmental researchers and policy-makers, Se is an important co-existing elemental component of the mineral matrix of Hg ore deposits in mercury mining areas. For instance, tiemannite (mercury selenide, HgSe) has been reported in Wanshan since 1975 (Bao, 1975; Zhang et al., 2012). Wanshan is known as the "mercury capital" of China; it once had the largest reserves and production of Hg in Asia and the third-largest reserves and production in the world (Zhang et al., 2010b, 2012). The chemical composition of the tiemannite from this area was measured as 70–74 wt% Hg and 24–27 wt% Se (Zhang et al., 2012). Selenium often occurs as an isomorphous substituent of sulfur in sulfide crystal lattices. Sulfur atoms in cinnabar ore can be replaced by Se atoms to form an isomorphous series of HgS–HgSe because the extremely high binding affinity between Se and Hg for mercury selenide (HgSe) is much greater than that for mercury sulfide (HgS) (Zhang et al., 2012). Therefore, cinnabar and ores in mercury mining areas typically contain considerable Se contents.

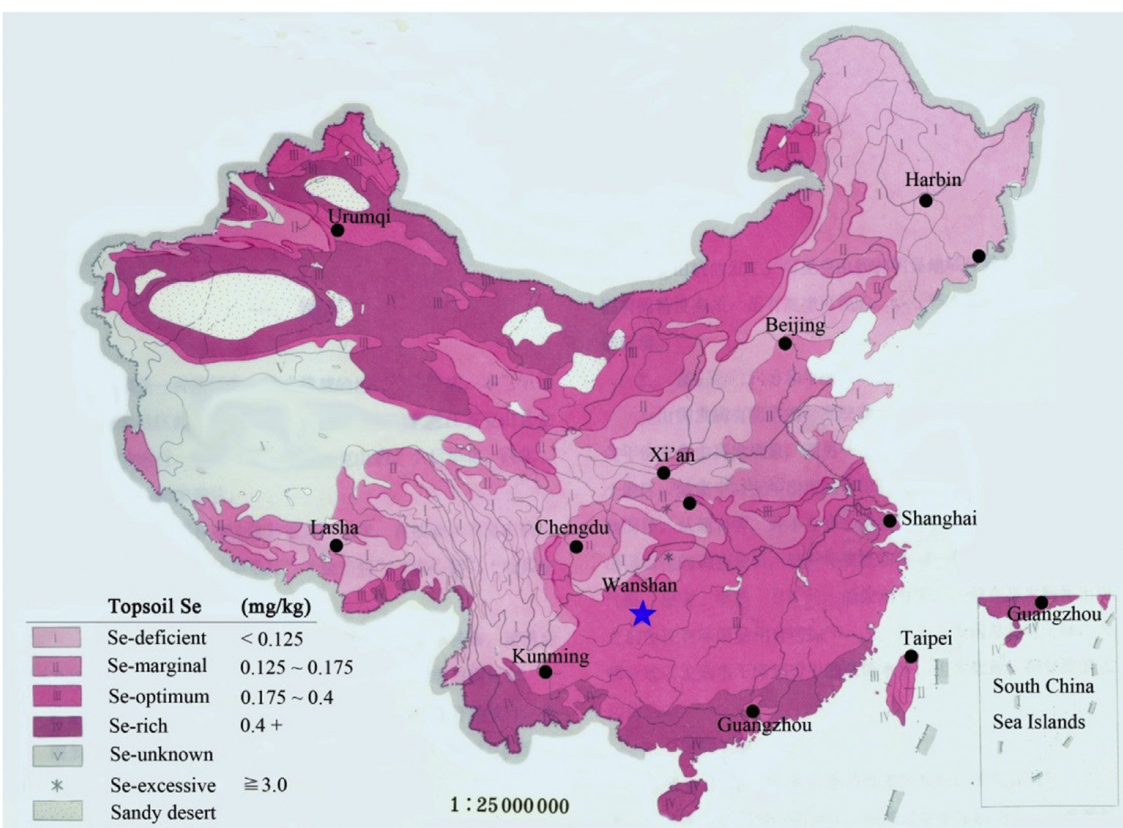

Fig. 1. Soil selenium distribution in China and the location of the study area (modified from that found in the literature; Tan, 1989).