Environmental Chemistry

Heavy metals in navel orange orchards of Xinfeng County and their transfer from soils to navel oranges

Jinjin Cheng a,b, Changfeng Ding a,b, Xiaogang Li a,b, Taolin Zhang a,b, Xingxiang Wang a,b,c,*

a Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, PR China
b University of the Chinese Academy of Sciences, Beijing 100049, PR China
c Jiangxi Key Laboratory of Ecological Research of Red Soil, Ecological Experimental Station of Red Soil, Chinese Academy of Sciences, Yingtan 335211, PR China

ABSTRACT

This study investigated heavy metal concentrations in soils and navel oranges of Xinfeng County, a well-known navel orange producing area of China. The results showed that the average concentrations of lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As) and mercury (Hg) in orchard soils all increased compared to the regional background values, especially for Cd, which increased by 422%. When compared to the Chinese Environmental Quality Standard for soil (GB15618-1995), Pb, Cr and Hg concentrations in all orchard soil samples were below the limit standards, but Cd concentrations in 24 soil samples (21%) and As concentrations in 8 soil samples (7%) exceeded the limit standards. However, concentrations of all heavy metals in navel orange pulps were within the National Food Safety Standard of China (GB 2762-2012). Dietary risk assessment also showed that the exposure to these five heavy metals by consumption of navel oranges could hardly pose adverse health effects on adults and children. Since the range and degree of soil Cd pollution was widest and the most severe of all, Cd was taken as an example to reveal the transfer characteristics of heavy metals in soil-navel orange system. Cd concentrations in different organs of navel orange trees decreased in the following order: root > leaf > peel > pulp. That navel oranges planted in the Cd contaminated soils were within the national food safety standard was mainly due to the low transfer factor for Cd from soil to pulp (TF pulp). Further studies showed that TF pulp was negatively correlated with soil pH, organic carbon (OC) and cation exchange capacity (CEC). Based on these soil properties, a prediction equation for TF pulp was established, which indicated that the risk for Cd concentration of navel orange pulp exceeding the national food limit is generally low, when soil Cd concentration is below 7.30 mg/kg. If appropriate actions are taken to increase soil pH, OC and CEC, Cd concentrations in navel orange pulps could be further reduced.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

With the development of a country’s economy and people’s living standards, improving the safety of agricultural products is a necessity for agriculture development. The contents of some heavy metals (Pb, Cd, Cr, As and Hg) in agricultural products are strictly limited by national standards in China (GB 2762-2012). These heavy metals are non-essential elements to biota and are among the most toxic environmental pollutants. They are known to be highly toxic to plants and animals even at relatively low concentrations (Khangarot and Ray, 1987; Nagajyoti et al., 2010). However, because of rapid industrialization and urbanization and the extensive application of agrochemicals, heavy metal pollution of soils has become an increasingly serious problem in China (Han et al., 2007; Wang et al., 2015). Heavy metals accumulated in agricultural soils may transfer to agricultural products and consumption of these agricultural products is one of the major exposure pathways for humans with regard to soil heavy metal contamination (Fang and Zhu, 2014). Therefore, an understanding of the transfer of these heavy metals from soils to agricultural products is very important.

The transfer factor (TF), which is expressed as the ratio of the heavy metal concentration in a plant to that in the soil, is an important parameter in the evaluation of the potential risk to human health for exposure to soil heavy metals (USEPA, 1992). There is general agreement that TF depends on many soil factors, such as soil pH, cation exchange capacity, clay content and organic matter content (Golla et al. 2008; Bošković-Rakocević et al., 2014). Based on these soil factors, a prediction equation can be developed to
quantify the transfer of a heavy metal from soils to agricultural products. Such a prediction equation belongs to the empirical model. It is easy to establish and can be used in many ways, such as human health risk assessment, soil thresholds derivation, cropping layout optimization and agriculture management (Ding et al., 2013). As an important part of the human diet, fruits can also accumulate toxic levels of heavy metals in their edible parts (Fang and Zhu, 2014). However, compared to vegetables and grains, prediction equations for heavy metals transfer from soils to fruits are rare in the literatures (Bi et al., 2010; Li et al., 2006).

Fruit trees generally are large in size and have relatively long juvenile periods. Therefore, developing prediction equations for fruits using controlled pot experiments is time consuming. To date, studies on heavy metals in fruits have generally been through market investigations (Radwan and Salama, 2006; Karavoltsos et al., 2008). These studies cannot explain the effects of heavy metals in the soil environment on fruit safety. In the aspect of field investigations, some studies only stay on the level of status quo description, and have not revealed the transfer characteristics of heavy metals in soil-fruit systems (Li et al., 2006; He et al., 2014).

Navel oranges are grown in 114 tropical and subtropical countries and are among the most economically valuable fruit crops in the world (Talon and Gmitter, 2008). Large amounts of phosphate fertilizers and organic materials are applied during the growth of navel orange trees, which may significantly increase the soil heavy metal concentration (Mulla et al., 1980; Canet et al., 1997) and therefore increase the trees’ heavy metal uptake. However, little information is available on heavy metal concentrations in different organs of navel orange trees or on the prediction equation for heavy metal transfer from soils to the edible portion of navel oranges.

Xinfeng County is an important orange production center in China. Researchers have reported that heavy metal contents in Xinfeng navel orange orchard soils are elevated after more than 30 years of development, and excessive levels of soil heavy metals are found in some navel orange orchards (Xue et al., 2013; He et al., 2014). Therefore, the present study uses Xinfeng County as an example to (1) investigate heavy metal concentrations in navel orange production system at the regional level and evaluate its safety; (2) reveal the major controlling factors and establish the prediction equation for the transfer of heavy metal from soils to navel orange pulps.

2. Materials and methods

2.1. Study area

The study area, Xinfeng County, is located in Ganzhou City in the Jiangxi Province of southern China (25°02′–25°23′ N, 114°39′–115°14′ E) and covers 2878 km². It is an important orange production center with a cultivated area of 13,000 ha and an annual output of 150,000 t in 2011. The major cultivar of navel orange is the Newhall navel orange (Citrus sinensis Osbeck cv. Newhall), which accounts for 88% of the entire navel orange planting area. This area has a subtropical, humid monsoon climate with a mean annual temperature of 19.6 °C and a mean annual precipitation of 1510 mm. The main soil types of navel orange orchards in this area are red soil derived from granite, quartzite and argillaceous rock (Ali-Udic Cambosols, Ali-Udic Cambosols and Argic-Udic Ferrosols, respectively according to Chinese Soil Toxonomy) and calcareous purple soil derived from purple gravel rock (Dystric Purpli-Udic Cambosols according to Chinese Soil Toxonomy).

This area has undergone rapid industrialization, especially for the mining and transport industry. There are approximately 15 coal mines in this county with an annual production capacity of 750,000 t. The Beijing–Kowloon railway and several national highways cross the county.

2.2. Soil and plant sampling

In late November 2012, 114 Newhall navel orange orchards (trees 8–12 years old, Citrus sinensis Osbeck cv. Newhall) were selected as monitoring sites for the study area (Fig. 1). In each orchard, 5 navel orange trees were selected according to S-shaped selecting principle. The trees all grew well with height and DBH (diameter at breast height) of 2.0–2.5 m and 9–10 cm. Under each tree, 4 soil points (about 200 g) were taken from a depth of 0–50 cm near the drip line in four directions. Besides, 4 fruits were collected from the external parts of the middle crown of each tree in four directions. Accordingly, 20 leaves were collected around where the fruits were collected. The fruits were mature with diameter of 70–80 mm and the leaves were spring-flush leaves. The roots (< 2 mm in diameter) were collected from a depth of 0–50 cm and were scooped up using a stainless shovel at the position where the soil sample was collected. All the soil or corresponding plant subsamples from each orchard were mixed as one soil or

Fig. 1. The locations of the soil sampling sites in Xinfeng County.
plant (fruit, leaf and root) sample, therefore, a total of 114 soil samples and corresponding plant samples were collected.

According to Lu (2000), all soil samples were air dried, milled to pass through a 2-mm sieve for pH, cation exchange capacity (CEC) and clay content determination, passed through a 0.25-mm sieve for analysis of organic carbon (OC) and passed through a 0.149-mm sieve for analysis of total soil concentrations of heavy metals (Pb, Cd, Cr, As and Hg) and Fe oxide (Feox). All plant samples were first washed with tap water, then scrubbed gently using a nylon brush in deionized water to remove superficial contamination, and finally rinsed thoroughly with ultrapure water obtained from a Milli-Q system (Millipore Corp., USA). The fruit samples were divided into pulp and peel, and the fresh weight of the pulp was recorded. Then, all plant samples were dried at 105 °C for 30 min and then at 75 °C in an oven until completely dry, after which they were ground and passed through a 0.25-mm sieve.

### 2.3. Soil and plant analysis

The soil physical and chemical properties were analyzed according to the routine analytical methods of agricultural chemistry in soil (Lu, 2000). Soil pH value, OC content, CEC, clay content (< 0.002 mm) and Fe oxide content are within the range of 3.75–8.23, 317–1728 g/kg, 5.08–35.83 cmol/kg, 6.76%–48.40% and 15.82–96.43 g/kg, and with averages of 5.06, 7.37 g/kg, 10.03 cmol/kg, 23.2% and 43.3 g/kg, respectively (Cheng et al., 2015). The soils were digested by HCl–HNO3–HF–HClO4 to determine the total contents of Pb, Cd and Cr and digested by aqua regia to determine the total contents of As and Hg. Plant samples were digested with a mixture of HNO3 and HClO4 for the determination of Pb, Cd and Cr and with HNO3–H2O2 (4:3) for As and Hg in high-pressure sealed digestion vessels according to the National Food Safety Standard of China (GB/T 5009.15-2003; GB/T 5009.11-2003). The Pb, Cd and Cr concentrations in the soil and plant digestion solutions were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700X, USA), and As and Hg concentrations were determined by atomic fluorescence spectrometry (AFS-610D2, Rayleigh, Beijing, China). A soil certified reference material (GBW07407, National Research Center for Certified Reference Materials, China) and a plant certified reference material, citrus leaf (GBW10020, National Research Center for Certified Reference Materials, China), were used to ensure the precision of the analytical procedure. The average recovery ratios of Pb, Cd, Cr, As and Hg in the reference soil were 98.2%, 99.1%, 102.5%, 103.6% and 97.9%, respectively, and the average recovery ratios of Pb, Cd, Cr, As and Hg in the reference plant were 99.3%, 96.9%, 109.1%, 98.5% and 101.5%, respectively.

### 2.4. Data analysis

The daily dietary intake of heavy metal through consumption of navel orange was calculated by following equation (Zhai et al., 2008):

$$\text{DIHM} = \frac{\text{DCNO} \times \text{HMC}}{\text{BW}}$$

(1)

where DIHM means daily intake of heavy metal; DCNO means daily consumption of navel orange which was chosen as 0.30 kg/d for adult and 0.10 kg/d for child; HMC means heavy metal concentration in navel orange pulp (based on fresh weight); and BW means body weight (60 kg for adult and 16 kg for child). The chosen of these parameters was based on field survey and USEPA exposure factors handbook (USEPA, 1997).

The transfer factor (TF) is used to evaluate the transfer efficiency of heavy metals from the soil to the plant, which is defined as the ratio of the heavy metal concentration in the plant to that in the soil. Therefore, the TFs of heavy metals from the soil to different organs of navel orange trees were calculated as follows:

$$\text{TF} = \frac{C_{\text{plant}}}{C_{\text{soil}}}$$

(2)

where TF (based on dry weight) is the transfer factor of the heavy metal from the soil to the root, leaf, peel and pulp of the navel orange tree, $C_{\text{plant}}$ is the heavy metal concentration in the root, leaf, peel and pulp of the navel orange tree, and $C_{\text{soil}}$ is the heavy metal concentration in the soil.

Pearson’s correlation analysis was conducted to determine the relationships between the different variables. To evaluate the effects of soil heavy metals on the fruit safety of navel oranges, stepwise multiple linear regression (SMLR) analysis was used to derive a prediction model for heavy metal transfer from soil to navel orange pulp with TF as the dependent variable and the soil properties as the independent variables. Using a SMLR methodology, only those factors that actually have effects on TF can be entered into the prediction equation.

Data were analyzed with the SPSS 18.0 and Sigma Plot 11.0 statistical packages. In developing the prediction equations, all data were log-transformed (except for pH) prior to analysis to fit their lognormal distributions.

### 3. Results

#### 3.1. Heavy metal concentrations in soils and navel orange pulps

Table 1 summarizes the heavy metal concentrations in the 114 navel orange orchard soils. A wide range of soil heavy metal concentrations was observed. According to the background values.
of heavy metals in soils of Ganzhou City, concentrations of all heavy metals in navel orange orchard soils increased. Especially for Cd, Cr and Hg, they increased by 422%, 76% and 75%, respectively. When compared to the Chinese Environmental Quality Standard for soil (GB 15618-1995), the total concentrations of Pb, Cr and Hg in soils were all below the maximum permissible concentration. However, Cd concentrations in 24 soil samples (21%) and As concentrations in 8 soil samples (7%) exceeded the national permissible limits.

The concentrations of the five heavy metals found in navel orange pulps were far lower than that found in soils (Table 1). All heavy metal concentrations in navel orange pulps were within the Maximum Levels of Contaminants in Foods indicated in the National Food Safety Standard of China (GB 2762-2012). For Cd, the maximum concentration of all 114 pulp samples was 0.005 mg/kg, which is only 1/10 of the limit value (0.05 mg/kg).

### 3.2. Dietary risk assessment through consumption of navel oranges

The daily dietary intake of heavy metals from navel oranges grown in Xinfeng County is shown in Table 2. Compared to the USEPA reference dose (RfDo), the mean daily intake of Cd was only 10% of the RfDo for both adult and child. The average intake of Cr was the highest, which was 30% and 38% of the RfDo for adult and child, respectively. Besides, the daily intakes of Pb, Cd, As and Hg from navel orange pulps were negligible. Therefore, the Pb, Cd, Cr, As and Hg exposure by consumption of navel oranges grown in Xinfeng County could hardly pose adverse health effects on adults and children.

### 3.3. Transfer of Cd from soils to the organs of navel orange trees

Table 3 shows Cd concentrations in different organs of navel orange trees. The highest Cd concentration occurred in the root, and the lowest Cd concentration was observed in the pulp. The mean Cd concentration in root was approximately 10 times greater than that in leaf, dozens of times greater than that in peel, and one hundred times greater than that in pulp. The transfer factor reflects the transfer efficiency of Cd from the soil to the orange. Among the different navel orange organs, the average TF values decreased in the following order: TFroot (7.75) > TFleaf (0.73) > TFpeel (0.13) > TFpulp (0.07) (Table 3).

### 3.4. Prediction equation for Cd transfer from soil to navel orange pulp

Pearson’s correlation analysis showed that the correlations of TFpulp with clay or Feox were not significant. However, TFpulp was significantly negatively correlated with pH ($r = -0.496, p < 0.01$), OC ($r = -0.268, p < 0.01$) and CEC ($r = -0.377, p < 0.01$). This indicates that the transfer efficiency of Cd from soil to navel orange pulp was lower with higher soil pH, OC and CEC.

Stepwise multiple linear regression analysis was performed to develop prediction equations for Cd transfer from soil to navel orange pulp:

$$ \log \text{TF}_{\text{pulp}} = -0.131 - 0.222 \cdot \text{pH}, \quad r^2 = 0.246, \quad p < 0.001 \quad (3) $$

$$ \log \text{TF}_{\text{pulp}} = -0.281 - 0.187 \cdot \text{pH} - 0.599 \log \text{CEC}, \quad r^2 = 0.298, \quad p < 0.001 \quad (4) $$

$$ \log \text{TF}_{\text{pulp}} = 0.626 - 0.178 \cdot \text{pH} - 0.578 \log \text{CEC} - 0.487 \log \text{OC}, \quad r^2 = 0.342, \quad p < 0.001 \quad (5) $$

According to Eqs. (3) and (4), approximately 25% ($p < 0.001$) of the variability in TFpulp was explained by pH, and the combination of pH and CEC could better explain the variability in TFpulp ($r^2 = 0.298, p < 0.001$). When pH, CEC and OC were all introduced into the equation, the accuracy of the prediction equation was significantly improved, with a determination coefficient of 0.342 (Eq. (5)).

The accuracy of the Eq. (5) was determined by plotting the calculated log TFpulp against the corresponding predicted log TFpulp (Fig. 2). Most of the calculated values for log TFpulp were within the 95% prediction intervals.

### 3.5. The application of the prediction equation

Because the Cd concentrations in all of the navel orange pulp samples were lower than the national food limit standard, back-calculation of soil threshold values from the prediction equation may not be accurate (Ding et al., 2013). However, three special cases were used to estimate the extent to which the soil is suitable...
for safe production of navel oranges. Case 1 is the worst case, with a minimum pH (3.75), OC (3.17 g/kg) and CEC (5.08 cmol/kg). Case 2 is the general case, with an average pH (5.06), OC (7.37 g/kg) and CEC (10.33 cmol/kg). Case 3 is the best case, with a maximum pH (8.23), OC (17.28 g/kg) and CEC (35.83 cmol/kg). These data were all measured values in this work. Plugging cases 1, 2 and 3 into Eq. (4), soil Cd concentration is equal to 1.87, 7.30 and 83.1 mg/kg in compliance with the national food limit, respectively.

4. Discussion

Compared to regional background values of soil heavy metals (Xue et al., 2013), concentrations of Pb, Cd, Cr, As and Hg in navel orange orchard soils all increased, indicating that there are inputs of exogenous heavy metals to navel orange orchard soils. According to the current situation of Xinfeng County, the inputs of exogenous heavy metals might be due to agricultural activities, traffic and mining, which have been identified as possible pathways for inputs of heavy metals to agricultural soils (von Hoffen and Saumel, 2014; Gurel and Basar, 2015; Niu et al., 2015). It’s worth noting that the range and degree of soil Cd accumulation was widest and the most severe. Most soils with excessive levels of Cd were distributed near coal mines and the county center, which was in agreement with previous investigations that mining activities and human activities in city, such as vehicle emissions and industrial discharges, could increase Cd concentrations in nearby soils (Gibson and Farmer, 1986; Cao et al., 2009).

In this paper, there were approximately 21% of the soils with excessive levels of Cd, but the Cd concentrations in all of the pulps were within the national food limit standard. This may be related to the relatively low transfer efficiency of Cd from soil to the navel orange pulp (TFpulp=0.07), which was much lower than that of vegetables (1.03) or rice (0.26) (Zhang et al., 2011). From the aspect of the navel orange tree itself, the TFpulp was approximately hundreds of times lower than TF value for Cd transfer from soil to navel orange root (TFroot), indicating that the root act as a barrier to the translocation of Cd within the navel orange tree (Davies and White, 1981). Therefore, only limited quantities of Cd (0.005–0.04 mg/kg, dry weight) can be transferred to navel orange pulps, which was similar to that found in other countries. For example, orange pulp Cd levels were 0.04, 0.007 and 0.001 mg/kg (dry weight) in markets in Egypt (Radwan and Salama, 2006), Greece (Karavolotos et al., 2008) and Brazil (Santos et al. 2004), respectively.

From the aspect of soils, previous studies have shown that the TF for Cd transfer from soils to plants varied significantly with certain soil properties for a given plant species (Wang et al., 2006; Zhang et al., 2014). In the present work, TFpulp was significantly negatively correlated with soil pH, OC and CEC. Stepwise multiple linear regression analysis also identified pH, OC and CEC as the main influencing factors for TFpulp. Soil pH controls the complexity and acid–base reactions of metal species, dissolution and precipitation of metal solid phases, and metal sorption, and generally has a significant negative correlation with the mobility and bioavailability of Cd (Hernandez et al., 2003; Fairbrother et al., 2007). Soil OC is a major contributor to the pH-dependent negative charge in soils, which gives rise to the soil’s ability to retain cationic metals (Stacey et al., 2010). Apart from soil pH and OC, soil CEC also play important roles in the retention of heavy metals in soils (Miner et al., 1997). Therefore, pH, OC and CEC as the main influencing factors for TFpulp was expected. However, using the same samples, we found that the transfer of rare earth elements from soil to navel orange pulp was significantly affected by soil pH, CEC and Feox (Cheng et al., 2015). Therefore, due to the difference in properties, the main influencing factors on the transfer of different metals from soil to navel orange pulp are different.

Based on the main influencing factors, prediction equation for TFpulp was established. The $r^2$ value (0.34) of the prediction equation in the present study was relatively low. Some higher $r^2$ values were obtained for other crops at the regional level and under field conditions. For example, the $r^2$ value of the prediction equation was 0.48 for Cd in rice (Wang, 2012) and 0.53 for Cd in wheat (Adams et al., 2004). The individual differences in the navel orange trees were higher than that of nettle and wheat, which may be a reason for the relatively lower $r^2$ value in our study. Moreover, a low $r^2$ value indicates that besides soil pH, OC and CEC, other factors must also significantly affect TFpulp. Previous studies showed that TF generally decreased with increasing soil metal concentration in certain range of Cd concentrations (Dudka and Miller, 1999; Zhang et al., 2014). Therefore, soil Cd concentration was one of factors that affected TF. In addition, samples in this work were collected under field conditions, and though they can reflect the real natural environment, they introduce many uncontrollable external factors, such as field topography, microclimate climate and human agricultural practices. These uncontrollable external factors may affect the transfer of Cd from soil to plant (Voutsas et al., 1996; Li et al., 2013; Zhang et al., 2014). Moreover, biotic factors, such as root activity and rhizosphere microorganisms, and non-biotic factors, such as accompanying anions and other metals, could also affect the transfer of Cd from soil to plant (Singh and McLoughlin, 1999).

Empirical models describing heavy metal transfer in soil-plant systems are needed to improve soil environmental quality standards. According to the prediction equation, there is very little risk for Cd contamination in navel orange pulp exceeding the national food limit when the soil Cd concentration is below 1.87 mg/kg. In general, when the soil Cd concentration is below 7.30 mg/kg, the risk of Cd concentrations in navel orange pulp exceeding the national food limit is still very low. Moreover, if appropriate actions are taken to increase soil pH, OC and CEC, Cd concentrations in navel orange pulp will not exceed the national food limit even when soil Cd concentrations are as high as 83.1 mg/kg. However, the current national soil standard value for Cd is 0.3 mg/kg, which is excessively strict for navel orange orchards and could limit the development of the navel orange industry. Therefore, further research is greatly needed to revise the current soil Cd standard for navel orange orchards. Besides, in terms of the food safety of navel oranges, the risk caused by soil Cd contamination is relatively low under current conditions. However, high concentrations of Cd in orchard soils may have adverse health effects on local residents by other exposure pathways, such as soil ingestion, inhalation and ground water drinking (Tripathi et al., 1997), which need to be further researched.

5. Conclusions

The average concentrations of Pb, Cd, Cr, As and Hg in orchard soils all increased compared to the regional background values. When compared to the national soil limit standards, Pb, Cr and Hg concentrations in all orchard soils were below the standards, but excessive levels of Cd and As were measured in some soils. The range and degree of soil Cd contamination was widest and the most severe. However, through dietary risk assessment and comparison with national food limit standards, the food safety risk of Pb, Cd, Cr, As and Hg in navel oranges of Xinfeng County was generally low. That navel oranges planted in the Cd contaminated soils were within the national food safety standard was mainly due to the low transfer factor for Cd from soil to pulp (TFpulp). Moreover, the TFpulp was significantly negatively correlated with soil pH, OC and CEC.
Acknowledgments

This work was supported by the Guangdong 555 Talents Program of Jiangxi (2012-3-58) Province, China, and the Knowledge Innovation Program of Chinese Academy of Sciences, PR China (IS-SASY112000016). The authors are very grateful to Mr. Liao Huiqiu and Mr. Lai Quanfu from the Agricultural Bureau in Xinfeng County, Jiangxi province, for their assistance in selecting the sampling sites.

Reference


