Environmental Pollution 235 (2018) 710–719

Contents lists available at ScienceDirect

Environmental Pollution

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

Bioavailability and soil-to-crop transfer of heavy metals in farmland soils: A case study in the Pearl River Delta, South China

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A R T I C L E I N F O

Article history:
Received 12 September 2017
Received in revised form
23 November 2017
Accepted 27 December 2017

Keywords:
Heavy metals
Farmland soil
Vegetable and rice
Bioavailability
Soil-to-crop transfer factor

A B S T R A C T

Soil-bound heavy metals are of great concern for human health due to the potential exposure via food chain transfer. In the present study, the occurrence, the bioavailability and the soil-to-crop transfer of heavy metals in farmland soils were investigated based on data from two agricultural areas, i.e. Sihui and Shunde in South China. Six heavy metals (As, Cu, Hg, Mn, Ni and Pb) were quantified in the farmland soils. The mean single pollution level indices (*PI*) were all lower than 1 except for Hg in soils from Shunde ($PI = 1.51 \pm 0.46$), suggesting the farmland soils were within clean and slightly polluted by heavy metals. As, Cu, Ni and Pb were found to be mostly present in the non-bioavailable form. The majority of Hg was considered potentially bioavailable, and Mn was found to be largely bioavailable. Soil pH was an important factor influencing bioavailability of soil-bound heavy metals. The concentrations of heavy metals in vegetables from Sihui and Shunde were within the food hygiene standards, while the rice grain from Sihui was polluted by Pb ($PI = 10.3 \pm 23.4$). Total soil concentrations of heavy metals were not correlated to their corresponding crop concentrations, instead, significant correlations were observed for bioavailable concentrations in soil. The results supported the notion that the bioavailability of the investigated heavy metals in the soil was largely responsible for their crop uptake. The soil-to-crop transfer factors based on bioavailable concentrations suggested that Cu, As and Hg in soils of the study area had greater tendency to be accumulated in the vegetables than other heavy metals, calling for further human health assessment by consuming the contaminated crops.

1. Introduction

Soil serves as a critical landscape for ecosystem and is the basic resource for food production, while soil is threatened by a large number of toxicants among which heavy metals are of great concern (Chen et al., 2015; Nannoni et al., 2011; O'Connell et al., 2008). Heavy metals in arable lands partially originated from natural sources, but in many cases they are from anthropogenic activities, such as fossil fuel combustion, mining, smelting, traffic, waste water irrigation and sewage sludge reuse, and the excessive application of pesticides and fertilizers (Lu et al., 2012; Temmerman et al., 2003). Soil-bound heavy metals in farmlands are likely to accumulate in agricultural products, e.g. vegetables and grains, which pose risks to human population which consume the polluted agricultural food or indirectly consume animals feeding on the agricultural products via the food chain (Chen et al., 2015; Liu et al., 2013; Nannoni et al., 2011; Sungur et al., 2014). Therefore, the transfer process of soil-bound heavy metals in soil-crop system has attracted increasing attention in recent years (Adamoa et al., 2014; Luo et al., 2011).

Accumulation of heavy metals from soil to plants mainly depends on the uptake mechanisms, the physicochemical properties of the soil and the chemical speciation of the metals and metalloids in soils (Kalembkiewicz and Palczak, 2005; Peijnenburg et al., 2007). Conventional risk assessment of soil-bound heavy metals is performed based on total metal concentrations in soils which

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https://doi.org/10.1016/j.envpol.2017.12.106
0269-7491/

may overestimate the risk (Hu et al., 2013; Li et al., 2004, 2014) and further result in the unnecessary and expensive soil remediation (Alexander, 2000; Kim et al., 2015; NRC, 2003). Conversely, the accumulation of heavy metals from soil to plants has been found to be better correlated with their bioavailable concentrations in soils (Adamoa et al., 2014; Kim et al., 2007). To date, studies on the bioavailability and transfer of heavy metals in soil-plant system mainly focused on the phytoremediation of soil in urban, mining and waste disposal sites using pot or field-plot experiments with limited sampling sites (Blanco et al., 2016; Vazquez et al., 2016). Several studies have assessed the bioavailability and transfer of heavy metals in soil-crop system in agricultural areas with specific pollution sources, e.g. mining and e-waste recycling sites, where the accumulation of heavy metals from soil to crops directly threatened human health via food consumption (Adamoa et al., 2014; Luo et al., 2011; Wang et al., 2012). However, limited information about the soil to crop transfer of potentially toxic metals and metalloids is available in the areas where residents are unaware of the potential metal pollution in farmland soils and consume local planting crops, which may cause broader exposure risk than those in the well-known severely polluted areas due to the unawareness.

The Pearl River Delta (PRD) is one of the most industrialized, urbanized and populous areas in China, and soil heavy metal pollution is one of the most concerning environmental issues in this region (Hu et al., 2013). A large number of studies have assessed the occurrence, distribution, fractionation and potential risk of heavy metals in soils in the PRD, with a focus on highly polluted areas, like mining sites (e.g. Zhuang et al., 2009) and e-waste recycling sites (e.g. Luo et al., 2011). However, attention has been scarcely paid on the bioavailability and soil-to-crop transfer of heavy metals in farmlands in remote areas, which was the main aim of the current study. Sihui and Shunde in the PRD were chosen as representative sites to fulfill the aim using the following steps: (1) to determine the concentrations of heavy metals in the farmland soils; (2) to determine the bioavailability of heavy metals in the soils and evaluate the influence of soil properties on the bioavailability; (3) to investigate the transfer of heavy metals in the soil-crop system based on their total and bioavailable concentrations in the soils. Sihui is located in the mid-west of Guangdong Province with agriculture, forestry and fishery as the primary industry. Shunde has experienced rapid transition from an agriculture-based economy to an industry-based economy during the last three decades (Li et al., 2009). Heavy metals have been detected in soils from Shunde (Cai et al., 2015, 2016), yet the bioavailability and soil-to-crop transfer of heavy metals in farmland soils are unknown. Therefore, Sihui and Shunde served as good representatives and comparisons to study the heavy metal pollution in farmland soils.

2. Materials and methods

2.1. Study area, sample collection and sample preparation

Soil samples were collected from agricultural areas of Sihui and Shunde in the PRD, South China, with a sampling area of about 77 km^2 and 50 km^2, respectively (Fig. 1). The study area is located in a subtropical climate zone with an average annual temperature and rainfall of 22.3 °C and 1832 mm, respectively and 83% of the rainfall is in the rainy season (from April to September) (SLRO, 2012). River alluvial deposits from the West River and North River are the main source of soil matters in the study area, resulting in extensive agricultural activities in the land (Cai et al., 2015). The river alluvial deposits are formed by the weathering of limestone, granite, quartz, shale and sandstone, and mainly consist of sand, clay and sandy clay. Soils in the study area are classified as paddy soil, stacked soil and lateritic red soil according to the classification and codes for Standardization Adminitration of the People's Republic of China (SAPRC, 2009). Rice, lettuce, pakchoi, lettuce, Chinese cabbage and flowering cabbage are the main crops cultivated in the study area. Comparatively, Shunde is more industrialized than Sihui.

A total of 68 surface soil samples (0–20 cm) together with 35 lettuce samples (the edible parts) and 31 rice grain samples were collected from agricultural fields in Sihui. In addition, 29 surface soil samples with 50 vegetable samples (Chinese cabbage, lettuce, rape, leaf lettuce, flowering cabbage and Chinese kale) were collected from the fields in Shunde (Fig. 1). Five sub-samples (soil, vegetable and rice grain) were collected within an area of 20 m^2 from each sampling site and mixed together to obtain a single composite sample. The samples (about 0.5 kg each) were placed in the plastic bags, transported back to the laboratory on ice and stored at −20 °C prior to analysis. The details of each site sample are presented in Tables S1 and S2 in the Supplementary Data.

The soil samples were dried at 60 °C for 72 h, sieved through a 2-mm nylon sieve (Jingxin Industrial Development Co., LTD, Shanghai, China) to remove sand, gravel and plant debris, and used for analyzing the soil pH and soil organic matter (OM). The pre-sieved soil was finely powdered by an agate ball-grinder (Jingxin Industrial Development Co., LTD) for 1 h using 10-mm agate balls, further sieved using a 74-μm nylon sieve and used for measuring the soil heavy metal contents (Hu et al., 2013).

The crop samples (vegetables and rice grain) were sequentially washed with tap water and de-ionized water, cut into small pieces with a stainless steel knife after drying at room temperature, and weighed and recorded as fresh weight. The plant samples were oven-dried at 85 °C for 30 min, kept in the oven at 60 °C for about two days until reaching a constant weight, weighed and recorded as dry weight (Wang et al., 2006). The plant moisture content was determined from the fresh and dry weights. Finally, the plant samples were grounded to fine powder using an agate ball-grinder, sieved through a 74-μm nylon mesh sieve, and stored in sealed plastic bags at room temperature prior to heavy metal analysis.

2.2. Chemical analysis

Total concentrations of heavy metals (As, Cu, Hg, Mn, Ni and Pb) in the soil and crop samples were analyzed after microwave digestion. Accurately weighed soil or crop sample (0.5 g) was digested with a mixture of concentrated nitric acid (15 mL) and hydrofluoric acid (5 mL) using a MARS microwave digestion system (CEM, USA) according to EPA method 3052 (USEPA, 1996). After evaporating the digested solution to near dryness, the residues were re-diluted to 50 mL with 1 M HNO_3.

Fractionation of the metals/metalloids of interest was obtained by a sequential extraction method (CGS, 2005). Heavy metals in the soil samples were successively extracted as the following seven fractions: water soluble fraction (F_1), ion-exchangeable fraction (F_2), fraction bound to carbonates (F_3), fraction bound to humic acid (F_4), fraction bound to Fe–Mn oxides (F_5), fraction bound to OM (F_6) and residual fraction (F_7). The detailed procedures of chemical fractionation are presented in the Supplementary Data.

The concentrations of heavy metals in the samples were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES; Optima 2000DV, Perkin Elemer, USA), except for As and Hg, which were analyzed by atomic fluorescence spectrophotometry (AFS-230, Beijing Haiguang Instrument Co., Ltd, Beijing, China) at a wavelength of 253.7 nm. The reporting limits of As and Hg in the soil and crop samples were 0.001 and 0.0001 mg/kg dry wt., respectively.

The pH of soil samples was determined by soaking a pH probe in