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Fractional distribution of thallium in paddy soil and its bioavailability to rice

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ABSTRACT

To investigate the bioavailability of thallium (Tl) in soil and rice in a Tl-contaminated area in Guangdong, China, the topsoil and rice samples were collected from 24 sampling sites and analyzed. Moreover, a modified sequential extraction procedure was applied to determine the different Tl fractions in the soil. The mean pH value of the soil samples was 4.50. The total Tl concentration in the paddy soil was about 4–8 times higher than the Canadian guideline value (1 mg kg^{-1}) for agricultural land uses. The mean ecological risk index of Tl was determined to be 483, indicating that potential hazard of the paddy soil was serious. The mean content of Tl in rice was 1.42 mg kg^{-1}, which exceeded the German maximum permissible level (0.5 mg kg^{-1}) of Tl in foods and feedstuffs by a factor of nearly 3. The hazard quotient value via rice intake was 57.6, indicating a high potential health risk to the local residents. The distribution of various Tl fractions followed the order of easily reducible fraction (40.3%) > acid exchangeable fraction (30.5%) > residual fraction (23.8%) > oxidizable fraction (5.4%). Correlation analyses showed that the easily reducible fraction correlates positively with the soil Fe and Mn contents, whereas the acid exchangeable fraction is significantly correlated with the S content. The soil pH was negatively correlated with the Tl content in both soil and rice. The Tl content in rice was more strongly correlated with the exchangeable fraction than the total Tl content in the soil. Overall, the bioavailability of Tl in more acidic soil is higher, and is strongly dependent on the speciation of Tl, especially the content of acid exchangeable fraction.

1. Introduction

Thallium (Tl) is a highly toxic and non-essential heavy metal element that has received relatively less attention on its environmental behavior compared to other metal elements (e.g., Hg, Pb, and Cd) (Xiao et al., 2012). This can be partially attributed to its low concentrations (0.1–1.7 mg kg^{-1}) in the earth's crust and difficulties in detection (Cvjetko et al., 2010; Peter and Viraraghavan, 2005), although it is distributed widely in the natural environment. Tl concentrations in typical environmental media are as follows: < 1.0 mg kg^{-1} in soil (Fergusson, 1990), < 0.036 μg L^{-1} in lake water (Lin and Nriagu, 1999), and < 0.3 mg kg^{-1} in edible plants (Kabata-Pendias and Pendias, 1992). However, with the development of mining, metal smelting, and chemical industry, large amounts of Tl is continuously released into the environment (Smith and Carson, 1977; WHO, 1996), resulting in serious regional Tl pollution. For instance, it was reported that discharge of mining wastes and smelter wastewater was blamed to have caused serious Tl pollution of Beijiang River (0.18–1.03 μg L^{-1}) and Xijiang River (0.22–0.40 μg L^{-1}), tributaries of Pearl River in Southern China (Xinhua News Agency, 2010, 2013). These two serious pollution accidents have aroused public concerns about Tl pollution in China.

Although both Tl^{+} and Tl^{3+} have been detected in the various environmental media (Lin and Nriagu, 1999; Rickwood et al., 2015; Twining et al., 2003), Tl^{+} is considered to be the predominant species of the metal in aqueous environments (Vink, 1993), which is also in accord with the standard electrode potentials of Tl ($Tl^{3+} + 2e \rightleftharpoons Tl^{+}$, $E^{\circ} = 0.77$ V). Tl^{+} has a similar radius as K^{+} (Hydrated ionic radius is

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1.49 Å for Tl^+ and 1.33 Å for K^+) (Downs, 1993). Consequently, Tl can easily substitute for K in biochemical processes of plants (Siegel and Siegel, 1976), and Tl^+ in soil is readily absorbed by crops (Renkema et al., 2012). Previous studies also confirmed that Tl tended to accumulate in food crops grown in Tl-polluted farmlands (Xiao et al., 2004). For instance, at Tl-polluted site in Lanmuchang, Southwest China, Tl contents ranged from 120 to 495 mg kg^{-1} in green cabbage, from 0.8 to 5.3 mg kg^{-1} in chili, from 0.87 to 5.4 mg kg^{-1} in Chinese cabbage, from 0.78 to 3.1 mg kg^{-1} in granular corn, and from 1.0 to 5.2 mg kg^{-1} in shelled rice (Xiao et al., 2004). High Tl contents were also detected in sweet potato (104.8 mg kg^{-1}), green cabbage (22.0 mg kg^{-1}), eggplant (8.6 mg kg^{-1}), taro (11.5 mg kg^{-1}), soybeans (1.2 mg kg^{-1}), and lettuce (14.2 mg kg^{-1}), which were grown in Tl-polluted soils near the Yunfu sulfuric acid plant in Southern China (Wang et al., 2013). In other countries, high Tl contents in crops grown in the Tl-polluted soils were also reported. For instance, high Tl levels were detected in the French gape seeds (33 mg kg^{-1}) (Tremel et al., 1997), in the Czech mustard shoots (65 mg kg^{-1}) (Vanek et al., 2010b), and in the German cereal grains (9.5 mg kg^{-1}) and green cabbage (45 mg kg^{-1}) (Dolgner et al., 1983). Previous studies indicated that the consumption of Tl contaminated agricultural products can pose serious risks to human health (Xiao et al., 2007; Zhang et al., 1998). Therefore, the studies on the biological availability and mobility of the toxic heavy metal Tl in the soil are of great significance.

The total metal concentration has been used as an important measure in assessing soil pollution and in establishing environmental quality standards and regulations in many countries. However, many studies have indicated that the chemical forms of heavy metals in soil and its binding form with soil can greatly affect the mobility, bioavailability, and toxicity of heavy metals in soil (Giller et al., 1998; Jin et al., 2005; Pedra et al., 2006; Peijnenburg et al., 2000; Tandy et al., 2009). Therefore, the total heavy metal content may not accurately reflect the actual toxicity, potential environmental impact, and the ability of plants absorption and accumulation of heavy metals (Antibachi et al., 2012; Li et al., 2009). To differentiate the availabilities of different fractions of metal species in soil, various operationally defined sequential extraction techniques are often employed to provide more accurate data on toxicity, mobility, and bioavailability of heavy metals (Lukaszewski et al., 2012).

Rice (*Oryza sativa* L.) is a dominant agricultural crop that provides the staple food for more than 60% of the world's population. China is the world's largest rice producer, accounting for approximately 20% of the cultivated area of rice in the world and 26% of all world rice production (Peng et al., 2009). However, with the rapid economic development and industrial activities over the last 3 decades or so, paddy soils contamination by heavy metals has become a serious environmental challenge in China. It was estimated that about 20% of the paddy soils in China is polluted by various heavy metals, while and most of the polluted soil is still cultivated due to a serious shortage of agricultural land (Chen, 2007). Over the past 15 years, many studies have investigated the mobility and bioavailability of heavy metals in paddy soils and their uptake and accumulation by rice plants. Yet, these studies have mainly focused on Cd, Pb, As, Cr, Cu, Zn, and Ni (Geng et al., 2017; Nagai et al., 2012; Xiao et al., 2015; Zhou et al., 2014). As a result, Tl speciation in paddy soil and its accumulation in rice plants remain unknown to date.

Therefore, the main objectives of this study were to: 1) determine the total concentration as well as the different fractions or chemical species of Tl in paddy soil in the Yunfu pyrite mining area, 2) measure the Tl content in rice grown at the Tl polluted soil, and 3) analyze the correlations between Tl concentrations in the paddy soil and rice with soil pH, and organic matter (OM) and identify how these factor affect thallium speciation and availability in the soil as defined by the modified BCR sequential extraction procedure.

2. Materials and methods

2.1. Description of the study site

Yunfu pyrite mine (112°0´ E, 22°58´ N) is the largest pyrite mine in China with a recoverable pyrite reserve of about 138 million tons. The mining area has been operated intensively since 1988. It discharges approximately 680,000 t of acid wastewater every year. A part of the untreated wastewater is discharged directly into the tailings ponds. Farmlands such as paddy fields are located near the tailings ponds. The irrigation of these farm lands depends heavily on the mining water from the tailings ponds. The local climate belongs to the subtropical monsoon, and the frost-free period is 350 days. The mean annual temperature is 21.5 °C. The annual precipitation is 1550 mm and 80% of the annual precipitation occurs mainly during the period from April to September. The abundant rain heat and long sunshine hours (1785 h annually) makes it conducive to the growth of rice.

The paddy soil and rice samples were collected from three different locations of the mining area. Sampling Site A is situated near tailing pond A (112°0´15" E, 22°59´31" N), Site B is near tailing pond B (111°58´21" E, 23°1´36" N), and Site C near tailing pond C (112°0´43" E, 23°0´49" N) respectively. Eight soil samples (S1–S8) were collected at Site A, 10 samples (S9–S18) from Site B and 6 (S19–S24) from Site C.

2.2. Paddy soil and rice sampling

Surface paddy soil samples (0–20 cm) were collected from the 24 sampling points after the rice harvest in November 2013. At the same time, grain samples were collected from the corresponding soil sampling spots of the paddy field. All the rice plants are the same species, and the growing conditions, such as irrigation, fertilization, climate, and rainfall, are similar. Soil and grain samples were kept in clean sealed polyethylene bags immediately and transported to the laboratory for further preparation and processing.

2.3. Sample preparation

All the 24 soil samples were air-dried for 3 months at room temperature and sieved through a 2-mm nylon sieve to remove stones and coarse debris. The sieved samples were collected and half of them were stored in polyethylene bottles for measurement of pH, organic matter (OM), and the Fe, Mn, Si, and S contents. The other half of them were ground again, passed through 0.149-mm nylon sieve and stored in polyethylene bottles for measurement of total Tl content and the sequential extraction analysis of various fractions of Tl in the soil.

The grain samples were washed with running tap water and deionized water in order to remove soil particles and air-dried for 1 day. Then, the grain samples were de-hulled with a ceramic pestle and mortar and oven-dried in an oven at 60 °C to constant weight, and then milled into a powder and passed through a 0.149-mm nylon sieve, and sealed in polyethylene bottles for later analysis.

2.4. Analytical methods

The paddy soil pH was determined in a 1:2.5 soil-to-water suspension with a calibrated pH meter (IQ150, Scientific Instruments, San Diego, CA, USA). Soil organic matter content was measured by the $K_2Cr_2O_7$-$FeSO_4$ method. The concentrations of Fe and Mn were determined by using Thermo Scientific ICE 3500 at. absorption spectrometer. The concentration of S and Si was determined by using PerkinElmer EA2400II elemental analyzer, and Prodigy Spectrum ICP-AES, respectively.

For total Tl analysis, 0.1 g of each soil sample was digested with 8 mL of 68% nitric acid (HNO_3, v/v) and 3 mL of 40% hydrofluoric acid (HF, v/v). 0.5 g of rice sample was digested with a mixture of HNO_3 (68%, v/v) and hydrogen peroxide (H_2O_2, 30%, v/v). The digestion