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Soil mercury speciation and accumulation in rice (*Oryza sativa* L.) grown in wastewater-irrigated farms

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ABSTRACT

Forty whole rice plants and corresponding rhizospheric soil samples were collected from rice paddy fields along four rivers in Tianjin, including three wastewater-irrigated areas [Beijing (BJR), Beitang (BTR) and Dagu (DGR) Wastewater Drainage River) and a control area (Haihe River (HHR)]. A sequential extraction technique was used for quantification of five mercury (Hg) fractions (soluble and exchangeable, specifically sorbed, oxide-bound, organic-bound and residual fractions) in the soil samples. Additionally, total Hg (THg) and methylmercury (MeHg) concentrations in soils and plants were measured using a DMA-80 direct Hg analyser and gas chromatography-cold vapour atomic fluorescence spectrometry (GC-CVAFS). The inorganic Hg (IHg) was calculated by subtracting the MeHg value from the THg value. Soil THg and MeHg concentrations were significantly higher in the wastewater-irrigated soils than those in the control area. Soil Hg was mainly found in the oxide-bound, organic-bound and residual fractions, the sum of which exceeded 98%. The average concentrations of THg and MeHg in seeds collected from the wastewater-irrigated areas ranged from 13 ± 7.3 to 28 ± 13 ng g^{-1} and from 4.5 ± 2.3 to 19 ± 11 ng g^{-1}, respectively. Rice grain accumulated the highest amount of MeHg rather than IHg. About 21% of MeHg intake through rice consumption presented a health risk to the local population in the four areas. Soluble and exchangeable Hg can be used to predict the THg and MeHg concentrations in the rice grains. If soluble and exchangeable Hg in paddy soil exceeds 0.0091 ng g^{-1}, the MeHg dietary intake may be above the permissible limit recommended by the United States Environmental Protection Agency.

1. Introduction

Mercury (Hg) is a major toxic pollutant and has received a great deal of attention due to its risks to human health. The accumulation, mobility and toxicological effects of Hg are strongly dependent on the chemical fraction and species (García-Ordiales et al., 2016; Baptista-Salazar et al., 2017). Of all the chemical species, methylmercury (MeHg) poses the greatest health threat to wildlife and humans due to its neurotoxicity and tendency to accumulate in the human brain (Antunes et al., 2016). Additionally, the average absorption rate of MeHg by the human body is about 95% (WHO, 1990). Consumption of seafood is currently regarded as the main pathway of MeHg exposure to humans.

Tianjin, which is located in northern China, is an important industrial base. Almost all the paddy fields have been contaminated by wastewater in the combined urban areas of Tianjin City, Beijing City and Hebei Province (Liu et al., 2007). Due to the shortage of clean irrigation water in these semiarid and arid zones, treated wastewater is an important source of irrigation in these areas. Wastewater has been the main source of irrigation for paddy fields in Tianjin for at least 50 years, which has led to large amounts of Hg in the terrestrial and aquatic ecosystems. Rice is the staple food for about half of the world's population; however, rice consumption is the main pathway of MeHg exposure to humans in mercury-mining areas and other areas in inland China (Feng et al., 2008; Zhang et al., 2010a, b).

Paddy fields are typically constructed wetlands and Hg is easily methylated to MeHg in the soil under these conditions (Meng et al., 2010, 2012). Flooded conditions favour the methylation of Hg by anaerobic bacteria and increase Hg and MeHg migration into the soil solution, causing elevated bioavailability of Hg and MeHg to rice plants (Peng et al., 2012). Previous studies have suggested that sulphur-reducing bacteria (SRB) is relatively abundant in rice paddy soil and have a high potential for Hg methylation (Zhou et al., 2015). Therefore, in the anoxic paddy soil environment, there is a high potential for Hg methylation.

The total heavy metal concentration is of little importance to its

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bioavailability in soils, and limited information has been provided for its bio-geochemical cycles and risks. Studies in mining areas have shown that MeHg and IHg in rice plants do not correlate with the total Hg (THg) concentrations in the soil (Rothenberg et al., 2011; Zhang et al., 2012), which may be due to the different bioavailable Hg fractions in the soil.

In this study, soil Hg fractions, as well as IHg and MeHg concentrations, in rice tissues collected from three representative wastewater-irrigated areas and a control area in Tianjin, north China, were studied. The aims of the study are: (1) to investigate the pollution status, accumulation and mobility of Hg in the wastewater-irrigated paddy soils; (2) to characterise the influence of different soil Hg fractions on the bioaccumulation of Hg in rice plants; and (3) to estimate the soil ecotoxicological risk and food safety.

2. Materials and methods

2.1. Study area

This study was conducted in Tianjin City, northern China, which is by the coast of the Bohai Bay, with an area of 1.1×10^4 km^2 (38° 15′ to 40° 14′ N, 116° 43′ to 118°03′ E). Tianjin is an important industrial base in China and its population was 1.47×10^8 in 2013. The total amounts of wastewater discharge were 2.04×10^8 and 4.08×10^8 m^3 for industry and household in Tianjin, respectively. In recent years, Hg release from anthropogenic sources has increased. Although large point-source discharges were eliminated by process optimisation or closures, the total emission has not reduced due to large quantities of coal being burned and emissions from non-coal sources (Wu et al., 2011). Therefore, a large amount of Hg was emitted into the atmosphere or aquatic environment, which then entered the terrestrial ecosystems by atmospheric deposition and agricultural irrigation.

The Tianjin wastewater-irrigated area consists of three parts: Beijing Wastewater Drainage River (BJR), Beitang Wastewater Drainage River (BTR) and Dagu Wastewater Drainage River (DGR) (Fig. 1). Therefore, these three catchments, as well as the Haihe River (HHR) catchment as the control site, were selected to determine the Hg distribution and accumulation in rice plants in agricultural areas. The information of each site is detailed in Table 1.

2.2. Sample collection and treatment

Whole rice plants and corresponding rhizospheric soil samples were collected from rice paddy fields downstream of the four river irrigation areas in the end of October 2014 (Fig. 1). All the samples were collected by composite sampling from the fields irrigated with wastewater and packed into zip-lock bags. Three subsamples of rice plants and soil were collected in a 4-m^2 area and then separately mixed the collected soils and rice plants together to obtain a bulk sample. Ten sets of samples were collected along each river basin paddy and 40 samples were obtained in total. Plant samples were washed thoroughly with tap water and then with deionised water. The collected rice plants were separated into subsamples of roots, stalks, leaves and grains and freeze-dried to constant weight. Soil samples were also freeze-dried. All the samples were crushed in a food blender and passed through a 100-mesh sieve and stored in polyethylene bags to avoid cross-contamination until chemical analysis.

2.3. Mercury in soils and rice plants

Total mercury concentrations in solid samples were measured using a DMA-80 direct Hg analyser (Milestone Ltd, Italy). All the samples were measured in triplicate and mean concentrations were obtained. For analysis of plant MeHg, 0.2-g samples were digested in 25% KOH/CH_3OH solutions for 3 h in a water bath at 75–80 °C (Liang et al., 1996). After cooling to room temperature, samples were acidified with concentrated HCl. For soil samples, a 0.2-g soil sample was prepared using $CuSO_4$/methanol solvent extraction. Next, methylene chloride was added to samples, which were then shaken, and MeHg was extracted. Polyethylene bottles were put in a water bath to back-extract MeHg from the organic phase into water, and then the aqueous phase was ethylated with sodium tetraethyl borate, purged with nitrogen gas and collected into a Tenax trap. The MeHg was then released with heat onto an isothermal gas chromatographic (GC) column, converted to elemental Hg by pyrolysis and analysed by a Brooks-Rand Model III CVAFS following US EPA method 1630 (2001). Inorganic Hg (IHg) was calculated by subtracting the MeHg value from the THg value.

There is no commonly accepted standard method of soil Hg fraction analysis. A sequential extraction technique based on the method of Zhou et al. (2015) was used in this study for quantification of the five Hg fractions. Briefly, the steps were as follows:

Soluble and exchangeable fractions were extracted with 1 mol L^{-1} $Mg(NO_3)_2$ (adjusted to pH 7 with HNO_3) from the soil samples. The sample was shaken for 1 h at room temperature and then centrifuged. The supernatant was transferred and the residue was washed with 10 mL of Milli-Q water.

The specifically sorbed fraction was extracted with 1 mol L^{-1} NaOAc solution (adjusted with HOAc to pH 5) from the residue of above step and then rinsed with another 10 mL of Milli-Q water. The detailed operational conditions were the same as those in the first step.

The oxide-bound fraction was extracted with 0.4 mol L^{-1} $NH_2OH{\cdot}HCl$ (dissolved in 25% HOAc) solution from the residue of above step and then rinsed with another 10 mL of Milli-Q water.

The organic-bound fraction was extracted with 30% H_2O_2 solution (adjusted to pH 2 with HNO_3) from the residue of above step and then rinsed with another 10 mL of Milli-Q water.

The residue of above step was freeze-dried and the Hg was measured by the DMA-80, and the measured concentrations are the residual fraction concentrations.

2.4. The probable daily intake (PDI) of MeHg

To estimate the MeHg intake from rice consumption, the PDI (μg kg^{-1} bw day^{-1}) values for adults were calculated as in Formula (1):

$$PDI = (C \times IR \times 10^{-3})/bw \quad (1)$$

where C refers to the MeHg concentrations in the rice in the four areas, bw refers to the bodyweight of an average adult in China (60 kg) and IR refers to the daily intake rate of rice (g d^{-1}). MeHg is not lost during cooking (Horvat et al., 2003). The daily IR of rice for the rural population (305 g d^{-1}) was adopted from the official data in the China Statistical Yearbook (NBS, 2015). The average body weight of 60 kg for the adult population was according to the second National Physique Monitoring Bulletin (GASC, 2005).

2.5. Quality assurance and quality control

For THg, instrument standard curves covering the appropriate absolute concentration were confirmed by soil reference (IGGE IRMA China, 590 ± 80 ng g^{-1}) and peach leaf standards (GBW08501, 46 ± 6 ng g^{-1}). To verify the accuracy of the THg analysis, quality assurance and quality control were conducted using duplicates, method blanks and certified reference materials (CRMs). The deviation, obtained from five duplicate measurements of the samples was 3.8% for soil and 3.3% for plant samples. The limit of instrument detection was 0.1 ng g^{-1} for solid samples and all the blanks were below the limit. CRMs were measured every ten samples, and the recoveries ranged from 96% to 105% for all the CRMs (Table 2).

For MeHg, quality assurance and quality controls were conducted using duplicates, method blanks, matrix spikes and CRMs (TORT-2 and IAEA-405). The standard deviation obtained from the five parallel