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Metal bioaccessibility in a wastewater irrigated soil-wheat system and associated human health risks: Implications for regional thresholds

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A R T I C L E I N F O

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A B S T R A C T

Accumulation of metal pollutants in soils and crops is putting increasing pressure on ecological function and human health. In the present study, the physiologically-based extraction test (PBET) was executed to determine bioaccessibility of Cd, Cu, Pb, Zn, Cr and Ni in soils and grains collected from a wastewater irrigated soil-wheat system. Furthermore, regional Cd thresholds in the agroecosystem were deduced based on the relationships among soil Cd, grain Cd and associated health risks. The results indicate that metal bioaccessibility vary among elements, with a mean range of 27.16–89.51% in soils and 18.53–87.96% in grains, respectively. Bioaccessibility of Cd, Cu, Pb and Zn in gastric phase (GB) are significantly greater than those in intestinal phase (IB) ($p < 0.05$); however, those of Cr and Ni vary with sample type (soils: GB > IB; grains: GB < IB). Linear regression analysis shows that strong correlations between total metals and bioaccessible metals are found for Cd, Cu, Zn and Ni in soils ($R^2 = 0.50$–0.99) and Cd and Zn in grains ($R^2 = 0.85$–0.99), while no significant correlations were found for other tested metals. Human health risks from bioaccessible metals via soil ingestion are negligible, while those via grain consumption are high, especially for Cd which accounts for 84.66% of the cumulative risks. To prevent associated health risks via grain consumption, values of 0.50 and 0.15 mg/kg are identified as regional Cd thresholds in the soils and grains, respectively. Our data provide an actual assessment of human health risks based on the PBET method, which facilitates the establishment of regional thresholds in the wastewater irrigated soil-wheat system.

1. Introduction

Metals can be categorized as essential and non-essential elements according to their necessity for organisms' growth and development. Essential elements (e.g., Cu and Zn) are elements that are required by organisms as enzyme activator or as constituents of prosthetic group, but elevated concentrations of these elements may cause detrimental effects on the organism (Naseri et al., 2015). Non-essential elements (e.g., Cd and Pb) are not required by organisms and can lead to serious health consequences even at low levels (Nordberg et al., 2002). With rapid industrialization and urbanization, pollution of essential and non-essential elements has become a critical issue in agroecosystem worldwide (Khan et al., 2013; Lu et al., 2015). Metal pollutants in farmlands can enter human body via occasional ingestion, inhalation and dermal contact of soil particles, where human health risks by metals via ingestion are 2–4 orders of magnitude higher than those from the other two routes (Li et al., 2015). More critically, soil metals can accumulate in edible parts of food crops posing major health concern to people (Khan et al., 2014). Thus, effective strategies are needed for regularly monitoring of metal pollution in agroecosystem.

Arable land per capita in China is below half of the world average, so protecting this precious resource from pollution is thus place very high in agenda of the Chinese government (Zhao et al., 2015). Metals of Cd, Ni, Cu and Pb are amongst the most significant pollutants in farmlands nationwide (MEP&MLR, 2014). To address this issue, the State Council of China approved official projects for comprehensive prevention and control of metal pollution in its 12th Five-Year Plan. One of the main objectives is to ensure the levels of metal pollutants in soils and crops below maximum permission concentrations in related environmental quality standards. Most of standards in operation, on the basis of total metal content, were enacted in the 1990s, e.g., GB15618-1995, GB13106-1991 and GB15199-1994. These standards had once played a crucial role in pollution control and food production, but it is gradually recognized that they are insufficient for diverse agroecosystem. Apart from total metal content, soil property (Zeng et al., 2011), microbial parameter (Xiao et al., 2017) and crop variety (Xing et al., 2016) also remarkably affect metal uptake by crops. Since these factors vary with location, transfer potential of metals from soils to

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grains and then to human body would be different among agroecosystem. This manifests that the standards suitable for one agroecosystem type may not satisfy others. Soil remediation, food production and health risk assessment under the guidance of improper thresholds may result in failure. In this regard, regional metal thresholds are very necessary in specific agroecosystem.

Numerous studies have evaluated human health risks of metals using total metal content (e.g., Huang et al., 2008; Si et al., 2011; Khan et al., 2013). The risks are overrated with such approach, since only bioaccessible metals are digestible by organism (Li et al., 2014). Bioaccessibility (or oral bioavailability) is defined as the fraction that can be released from matrix into gastrointestinal tract during the process of digestion (Oomen et al., 2002). It stands for the maximum of metals reaching systemic circulations of consumers (Fu and Cui, 2013), and is used for better understanding of actual health risks (Xia et al., 2016). Hence, an increasing number of researches pay more attention on health risk assessment with the aid of bioaccessible metal concentration (Li et al., 2014; Omar et al., 2015; Praveena and Omar, 2017). Bioaccessibility generally varies with sample and element, indicating that site-specific investigation is required (Oomen et al., 2002). In practice, feasibility of executing in vivo studies is challenged by time-consuming and high-cost methods (Van de Wiele et al., 2007). The alternative is using *in vitro* protocols that enable rapid, inexpensive and efficient measurement. The physiologically-based extraction test (PBET) initially developed by Ruby et al. (1996) was applied for bioaccessibility of Pb and As in solid matrixes (e.g., mine wastes, residential soils, tailing samples, stream channel samples and house dusts). Shortly afterwards, the PBET method has been successfully applied for various metals in a variety of plant samples, such as wheat grains (Chan et al., 2007), vegetables (Intawongse and Dean, 2008) and rice grains (Zhuang et al., 2016), probably partially because the PBET results were validated in *in vivo* study (Ruby et al., 1996).

This study is part of a large experiment exploring the transfer characteristic of Cd, Cu, Pb, Zn, Cr and Ni in the soil-grain-human continuum near a long-term mining and smelting area. Our previous results shows that metal bioaccessibility is a reliable indicator for elucidating their transfer in the continuum (Liu et al., 2017). However, associated health risks derived from bioaccessible metals are not clear, and whether regional thresholds could be deduced with the aid of metal bioaccessibility has not yet been sufficiently studied. The main objectives of this study are: (1) to determine bioaccessibility of these metals in the soils and wheat grains using the PBET method; (2) to evaluate associated human health risks from soil ingestion and grain consumption; and (3) to deduce regional metal thresholds in both soils and grains. Information from this study will provide better guidance for pollution control and food security in wastewater irrigated agroecosystem worldwide.

2. Materials and methods

2.1. Study area and sampling

Dongdagou watershed (104°12′-104°25′ E, 36°24′-36°35′ N) (Fig. S1), a small but important region in the upper Yellow River, Baiyin district, NW China, is well-known for metal mining and smelting industry. The watershed is named after Dongdagou stream (~38 km) which stems from an open-pit mine (104°15′ E, 36°39′ N), receives industrial effluent from close-by plants and finally discharges the wastewater into the Yellow River. Due to a lack of precipitation (180–450 mm/year), irrigation using wastewater from the Yellow River and Dongdagou stream has long been a common practice in this region (Cao et al., 2016). Our data showed that mean concentrations of Cd and Pb in water sample from Dongdagou stream were 0.08 and 0.51 mg/L for each, exceeding the maximum permissible levels of pollutants according to the Chinese national standards for irrigation water quality (GB5084-2005) by 8.00- and 2.55-fold, respectively (data unpublished). As a result, this watershed become a typical wastewater irrigated area, where both the soils and crops are seriously contaminated with heavy metals, especially Cd (Nan and Zhao, 2000; Li et al., 2006; Kong et al., 2014; Liu et al., 2016a). For this reason, in 2015, Baiyin district was officially identified as the first among 30 regions nationwide for the prevention and control of metal pollution funded by the Chinese government.

Table 1
General information of Dongdagou watershed, Baiyin district. [a] and [b], values are compiled from our previous studies (Liu et al., 2016a, 2017). MAT: mean annual temperature; MAR: mean annual rainfall; MAE: mean annual evaporation; SOM: soil organic matter.

Analysis	Values	
Coordinate	104°12′–104°25′ E	36°24′–36°35′ N
Area (km^2)	236	
Altitude (m)	1296–2992	
MAT (°C)	6–9	
MAR (mm)	180–450	
MAE (mm)	1500–1600	
Soil property[a]		
Order	Sierozem (or Aridisol)	
Texture	Sandy loam	
pH (H_2O)	7.66–8.82	
SOM (%)	0.38–2.78	
Clay (%)	3.61–18.79	
Silt (%)	32.39–79.68	
Sand (%)	12.55–63.99	
Total metal content[b]	Soils	Wheat grains
Cd (mg/kg)	6.96–56.59	0.46–4.99
Cu (mg/kg)	255.3–444.5	5.40–9.37
Zn (mg/kg)	215.2–406.9	48.40–106.3
Pb (mg/kg)	150.4–235.0	0.44–1.69
Cr (mg/kg)	0–39.24	0–2.12
Ni (mg/kg)	18.18–67.87	0.23–0.52

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General information about this region is summarized in Table 1. The soils tested are categorized as sierozem (or aridisol in USA soil taxonomy), with a sandy loam texture and varying clay (3.61–18.79%), sand (32.39–79.68%) and silt (12.55–63.99%). Soil pH ranges from 7.66 to 8.82, and soil organic matter is in the range of 0.38–2.78% (Table 1). Local wheat belt (104°12′ E, 36°32′ N) is situated at the upstream of Dongdagou stream, close to the mining and smelting site (Fig. S1).

Based on our early investigation and in order to obtain a broad range of soil metal contents, 12 sites were selected on the basis of their distances from Dongdagou stream. To determine bioaccessibility of Cd, Cu, Pb, Zn, Cr and Ni in the soil-wheat system, paired samples of soils and wheat grains (0–20 cm depth) were collected during the maturity period of wheat crop (June 2015). At each sampling site, five subsamples (~200 g), one from the center and four from the margin of a $10 \times 10\ m^2$ plot, were collected and mixed into a composite sample. In total, 12 paired composite samples of soils and wheat grains were obtained from the soil-wheat system.

2.2. Chemical analysis

All samples were processed and analyzed in the Key Laboratory of Biomonitoring and Bioremediation for Environmental Pollution, Gansu province, China. The details of sample pre-treatments followed Liu et al. (2017). Analysis of total metal content in samples was prepared as follows: 0.3 g samples of soils (particle size < 149 μm) were digested with 10 ml mixture of concentrated HNO_3-HF-$HClO_4$ (5:4:2, v/v/v), and 0.5 g samples of grains (fine ground) were digested with 10 ml mixture of concentrated HNO_3-$HClO_4$ (5:2, v/v). After dilution to a volume of 25 ml, total contents of Cd, Cu, Pb, Zn, Cr and Ni in the