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Coupling bioavailability and stable isotope ratio to discern dietary and non-dietary contribution of metal exposure to residents in mining-impacted areas

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ABSTRACT

Both dietary and non-dietary pathways contribute to metal exposure in residents living near mining-impacted areas. In this study, bioavailability-based metal intake estimation coupled with stable Pb isotope ratio fingerprinting technique were used to discern dietary (i.e., rice consumption) and non-dietary (i.e., housedust ingestion) contribution to As, Cd, and Pb exposure in residents living near mining-impacted areas. Results showed that not only rice (n = 44; 0.10–0.56, 0.01–1.77, and 0.03–0.88 mg kg^{-1}) but also housedust (n = 44; 2.15–2380, 2.55–329, and 87.0–56,184 mg kg^{-1}) were contaminated with As, Cd, and Pb. Based on in vivo mouse bioassays, bioavailability of As, Cd, and Pb in rice (n = 11; 34 ± 15, 59 ± 13, and 31 ± 15%) were greater than housedust (n = 14; 17 ± 6.7, 46 ± 10, and 25 ± 6.8%). Estimated daily intake of As, Cd, and Pb after incorporating metal bioavailability showed that As intake via rice was 5-fold higher than housedust for adults, whereas As intake via housedust was 3-fold higher than rice for children. For both adults and children, rice was the main source for Cd exposure, while housedust was the predominant Pb contributor. To ascertain the dominant Pb source from housedust ingestion, stable Pb isotope ratios ($^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$) of hair samples of local residents (n = 27, 0.8481 ± 0.0049 and 2.0904 ± 0.0102) were compared to housedust (n = 27, 0.8485 ± 0.0047 and 2.0885 ± 0.0107) and rice (n = 27, 0.8369 ± 0.0057 and 2.0521 ± 0.0119), showing an overlap between hair and housedust, but not rice, confirming that incidental housedust ingestion was the main source of Pb exposure. This study coupled bioavailability and stable isotope techniques to accurately identify the source of metal exposure as well as their potential health risk.

1. Introduction

In mining-impacted areas, As, Cd, and Pb often exist as co-contaminants, resulting in adverse health effects including cardiovascular disease, decreased bone density, neuro-behavioral effects, and even cancers (Naujokas et al., 2013; Riederer et al., 2013; Navas-Acien et al., 2007; Oliver-Williams et al., 2018). For residents living near mining-impacted areas, both dietary and non-dietary pathways are important contributors to metal exposure (Li et al., 2011; Zheng et al., 2013).

Metal-contaminated dust particles from mining activities could deposit on indoor surfaces of nearby houses via atmospheric deposition, leading to incidental ingestion of housedust by residents especially for children with hand-to-mouth behavior (von Lindern et al., 2016). Li et al. (2015) reported the contribution of housedust ingestion to blood Pb in children living near industrial areas. In addition, studies also reported elevated As and Cd concentrations in foods from mining areas such as rice (Hu et al., 2016; Chen et al., 2018a, b). As a staple food for the vast population in Asia, rice is a significant contributor to As and Cd intake (> 70%) (Torres-Escribano et al., 2008; Zhu et al., 2016). However, for residents living near mining-impacted areas, the contribution of dietary and non-dietary pathways to metal exposure needs to be clarified, which helps to develop targeted interventions to reduce metal exposure and the associated health risk.

To differentiate dietary from non-dietary pathways, one method is to estimate daily metal intakes from foods and environmental media using bioavailability-based methods. Bioavailability assessment is critical to determine the fraction of metals in food and environmental matrices that are solubilized in gastrointestinal fluid and absorbed

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across the gastrointestinal epithelium into the systemic circulation (Ruby et al., 1999). The inclusion of metal bioavailability into human health exposure assessment helps to refine the default assumption that external dose is equivalent to the internal dose. In reality, the physicochemical parameters of contaminants and the matrix both influence metal dissolution and absorption, thereby impacting the extent of the internal dose. However, assessment of metal bioavailability in contaminated housedust and rice samples from mining-impacted areas is not routinely undertaken. While studies have developed in vivo mouse bioassays to assess As and Cd relative bioavailability (RBA, relative to sodium arsenate and cadmium chloride) in rice samples (Li et al., 2017; Zhao et al., 2017a, 2017b), there is no report of Pb-RBA in rice. Though studies reported As- and Pb-RBA of 22–86% and 29–60% in housedust from urban areas (Li et al., 2014a, 2014b), there is a lack of measurement of As-, Cd-, and Pb-RBA in mining-contaminated housedust. More importantly, co-contaminants in rice or housedust may interact with each other, thereby impacting their RBA (Ollson et al., 2017). To gain a comprehensive understanding of metal exposure and the contribution of dietary and non-dietary pathways, assessment of As-, Cd-, and Pb-RBA in rice and housedust is essential.

Although the approach of estimating daily metal intakes could discriminate between dietary and non-dietary contribution, it also has uncertainties with the assumption of daily rice consumption and housedust ingestion rates, which could vary considerably among individuals. In addition, the internal metal dose is also influenced by individuals' nutrient status (e.g., intake of minerals like Ca, Fe, and Zn), which is not considered by bioavailability-based metal intake method. Furthermore, stable isotope ratio technique can be used as a supplementary measure to identify the source of metal exposure from foods and environmental media using internal biomarkers (e.g., blood, hair, and urine). Li et al. (2015) used stable Pb isotope ratio technique to identify the dominant source of Pb in children's blood. By coupling bioavailability-based intake estimation and stable isotope ratio method, dominant exposure sources (dietary vs. non-dietary) can be more accurately assessed.

Therefore, the objective of this study was to assess the contribution of dietary and non-dietary pathways to metal exposure in residents living near mining-impacted areas by coupling bioavailability-based metal intake estimation and stable isotope ratio fingerprinting. Typical mining-impacted areas in Hunan, China were selected and housedust, rice, and hair samples were collected from local residents. Rice and housedust were selected as the representative of dietary and non-dietary contributors to metal exposure. Following determination of metal concentrations, rice and housedust samples were measured for As-, Cd- and Pb-RBA using in vivo mouse assays. Estimated daily intake of As, Cd, and Pb via rice consumption and housedust ingestion was calculated to identify the dominant metal exposure source. In addition, to verify Pb source, stable isotope ratios of Pb in residents' hair were compared to those of rice and housedust samples. This study coupled bioavailability with stable isotope techniques to accurately identify the source of metal exposure as well as their potential health risk assessment, which is valuable to effectively reduce metal exposures to residents living near mining-impacted areas.

2. Materials and methods

2.1. Sampling and processing of rice, housedust, and human hair

Mining-impacted areas in Chenzhou and Hengyang cities in Hunan, China were chosen as the study site (Fig. 1). Hunan is a major rice producing area with > 4000 ha of paddy fields (Williams et al., 2009), however, it is also the heartland of mining/smelting activities. Numerous studies documented elevated As, Cd, and Pb concentrations in paddy soils and rice in Hunan (Zhu et al., 2008; Liao et al., 2005). Williams et al. (2009) reported that As, Cd, and Pb concentrations in rice grains from mining districts in Hunan were 0.15–0.59, 0.03–2.76, and 0.05–0.78 mg kg^{-1}, while Liu et al. (2005) reported As, Cd, and Pb concentrations at 82.0–1227, 1.7–11.1, 42.2–1444 mg kg^{-1} in soils from Pb/Zn mine areas of Hunan. A recent paper also showed high As, Cd, and Pb concentrations in farmland soils at 23.7–148.7, 0.24–3.83, and 35.1–173.7 mg kg^{-1} from mining-impacted areas of Hunan, suggesting that metal contamination at mining areas (Zhuang et al., 2018).

From the two cities, six locations were chosen as study sites, i.e., Wugaishan Mountain, Matian, Zilong, and Dengjiatang villages from Chenzhou, and Zhupo and Yancheng villages from Hengyang (Fig. 1). From the 6 sites, paired rice (polished, locally-grown) and housedust samples (n = 44) were collected. Rice was selected to represent dietary contributor to metal exposure, while vegetable samples were not. This was because most residents consumed vegetables not locally-grown. In addition, drinking water was not contaminated with metals at the sites so it was not included. All rice samples were locally-grown and were consumed by local residents.

Housedust on indoor surfaces including floors, window sills, and furniture was brushed into plastic sample bags and sealed. Outdoor soil was not considered since adults and children spend more time indoors with their propensity for hand to mouth contact with housedust compared to soils. In addition, hair samples were collected from 27 participants aged from 3 to 80 years who consumed rice as a staple (Table S1), with scalp hair being sampled from the occipital region of the head using scissors and stored in sealed plastic bags. Although there are limitations in using element concentrations in hair as biomarkers of exposure to metals (Skröder et al., 2017), hair has been used widely as a biomonitor after careful washing (Hinwood et al., 2003; Cui et al., 2013). Participants were asked to complete a self-administered questionnaire including information regarding age, sex, and body weight (Table S1).

To prepare samples for analysis, rice was washed thoroughly with Milli-Q water three times to remove dust particles. Following washing, rice was cooked using an electric cooker (CFXB50YB7F-65, Supor, China) at a ratio of rice to water of 1:2. After cooking, rice was stored at −80 °C and freeze-dried (Freezone 6 Plus, Labconco, USA) prior to grinding to a powder for homogenization. Housedust was freeze-dried, thoroughly mixed, and sieved to < 150 μm for further analysis. This fraction was selected since it is most likely to adhere to children's hands and be ingested via hand-to-mouth contact (Ruby and Lowney, 2012). Hair samples were cut into 5 mm pieces, washed in three steps using Milli-Q water, methanol, and Milli-Q water, then dried at 60 °C. The water-methanol washing method is efficient to remove surface hair contamination without leaching internal metals of interest out of the hair (Hinwood et al., 2003; Cui et al., 2013). Concentrations of As, Cd, and Pb in rice, housedust, and hair were determined using inductively coupled plasma mass spectrometry (ICP-MS, NexION300X, PerkinElmer, USA) following digestion using a Hot Block digestion system (Environmental Express, Mt. Pleasant, SC) according to USEPA Method 3050B.

In addition to total As analysis, As speciation in cooked rice was determined according to Zhu et al. (2008). Briefly, cooked rice powder (0.5 g) was extracted using 1% nitric acid (10 mL) in a microwave-accelerated reaction system (ETHOS UP, Milestone Srl, Italy). Samples were heated to 55 °C for 10 min, then 75 °C for 10 min, and finally 95 °C for 30 min. After cooling to room temperature, extracts were centrifuged, filtered through 0.22 μm filters, diluted with 1% nitric acid, and assessed for As speciation using HPLC-ICP-MS. An anion exchange chromatography column (Hamilton, PRP-X100, 250 mm × 4.1 mm, 10 μm particle size) was used as the mobile phase to separate As species using 8.0 mM $(NH_4)_2HPO_4$ and 8.0 mM NH_4NO_3 (pH = 6.2). Standard solutions of arsenite (AsIII), arsenate (AsV), dimethylarsinic acid (DMA), and monomethylarsonic acid (MMA) were prepared daily from stock solutions. A standard of 10 μg As L^{-1} was measured every 10 samples to monitor the stability of HPLC-ICP-MS, showing recovery of 95.1 ± 3.5%. The extraction efficiency of the 1% nitric acid method was 78.2–95.7%, averaging 87.2 ± 7.46%. The sum of AsIII and AsV