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Assessment of cadmium bioaccessibility to predict its bioavailability in contaminated soils

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ABSTRACT

In vitro assays have been developed to determine metal bioaccessibility in contaminated soils; however, their application to Cd is limited. To assess their suitability to determine Cd relative bioavailability (RBA), Cd-RBA in 12 contaminated soils containing 3.00–296 mg kg^{-1} Cd were determined using a mouse model and compared with Cd bioaccessibility data based on four assays including the UBM, SBRC, IVG, and PBET. After being administered feed amended with soil or $CdCl_2$ for 10-day, the Cd concentrations in the mouse liver and/or kidneys were used as biomarkers to estimate Cd-RBA. Cd-RBA was comparable at 34–90% and 40–78% based on mouse liver and kidneys with RSD of 7.10–8.99%, and 37–84% based on mouse liver plus kidneys with lower RSD of 5.8%. Cadmium bioaccessibility in soils varied with assays, with 61–99, 59–103, 54–107, and 35–97% in the gastric phase and 20–56, 38–77, 42–88, and 19–64% in the intestinal phase of the UBM, SBRC, IVG and PBET assays. Based on the combined biomarker of liver plus kidneys, better correlation was observed for PBET (r^2 = 0.61–0.70) than those for IVG, UBM and SBRC assays (0.12–0.52). The monthly Cd intake in children was 0.24–23.9 μg kg^{-1} using total Cd concentration in soils, which was reduced by 43% to 0.18–12.3 μg kg^{-1} using bioavailable Cd. Our data suggest it is important to consider Cd-RBA to assess risk associated with contaminated soils and the PBET may have potential to predict Cd-RBA in contaminated soils.

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1. Introduction

With rapid urbanization and industrialization over the past three decades, heavy metal contamination in soils has become an issue in china (Li et al., 2014; Wang et al., 2001). Recent nationwide surveys showed that cadmium (Cd) contaminated soils account for up to 7% of contaminated soils based on the Chinese Soil Environmental Quality Standards, making it most serious problem in China (Zhao et al., 2015). This is partially due to the low Cd class II values (0.3 mg kg^{-1} for soils with pH < 7.5), which is to protect agricultural production and human health via food chain, and is applicable to agricultural, orchard and pasture land. Cadmium concentrations in soils in England and Wales are also high, with 45% > 0.3 mg kg^{-1}, but they are within their guideline values (residential soil = 10 mg kg^{-1}) (Rawlins et al., 2012). Cadmium in soils derives from both anthropogenic and geogenic origins. Mining and smelting of ores, atmospheric deposition from incineration, and burning of fossil fuels are the main contributors to Cd in contaminated sites (Alloway 1995).

Human exposure to Cd can result in obstructive pulmonary disease, emphysema, and kidneys disease (Faroon et al., 2012). Its exposure pathways include smoking, consumption of contaminated food or water, inhalation of dust, and incidental ingestion of Cd-contaminated soil and dust. For children living near contaminated sites, soil ingestion may be an important pathway (Schilderman et al., 1997). In vivo experiments based on mouse and swine models showed that not all the Cd in soils is absorbed into systemic circulation and becomes bioavailable, which means Cd bioavailability is often <100%. Therefore, using total Cd in soils to perform risk assessment may overestimate its risks.

To refine Cd risk from oral ingestion of contaminated soils, animal model using juvenile swine and mouse have been used to estimate Cd relative bioavailability (RBA) (Denys et al., 2012; Juhasz et al., 2010). However, animal models are costly and time consuming. As a result, UBM (unified BARGE method), SBRC (Solubility Bioaccessibility Research Consortium), IVG (in vitro gastrointestinal) and PBET (physiologically based extraction test) assays have been developed to simulate gastrointestinal process in humans (Denys et al., 2012; Juhasz et al., 2010; Ruby et al., 1996; Schroder et al., 2003). The fraction of Cd dissolved in gastrointestinal fluids represents the Cd potentially

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available for absorption into the systemic circulation, i.e., bioaccessible Cd.

Even though these assays have been used to determine metal bioaccessibility in soils, inconsistent results have been found using different methods. For example, different Cd bioaccessibility in the gastric phase of SBRC (57–122%), IVG (43–107%), and PBET (30–110%) was found in 7 Cd-contaminated soils partially due to their different gastric pH values (Juhasz et al., 2010). Oomen et al. (2002) found different Cd bioaccessibility in 3 soils using 5 in vitro assays. Similar results were found for Pb bioaccessibility in contaminated soils by Li et al. (2015a) who reported that Pb bioaccessibility was significantly higher using the gastric phase of SBRC (3.0–99%) than those of the UBM, IVG, and PBET assays (0.46–84%). This may be due to different compositions and extraction parameters in different assays such as pH and soil/solution ratio.

In addition, in vitro assays must be predictive of in vivo RBA before being used as an appropriate surrogate. To date, several studies showed good correlation between Cd bioaccessibility and Cd bioavailability in contaminated soils. For example, Schroder et al. (2003) found a good correlation ($r^2 = 0.64$) between Cd bioaccessibility based on the IVG assay and Cd bioavailability based on the Cd concentrations in the kidneys following 15-day of dosing of 10 soils to juvenile swine. Cadmium bioaccessibility using the UBM is strongly correlated ($r^2 = 0.77$–0.94) with Cd-RBA based on the Cd concentrations in the liver, kidneys, femur or urine of juvenile swine following 14-day of dosing of 10 soils (Denys et al., 2012). Bioaccessible Cd using the SBRC and PBET assays is also correlated ($r^2 = 0.72$–0.91) with Cd-RBA based on the Cd concentrations in the liver or kidneys using a mouse model (Juhasz et al., 2010). However, limited studies focus on the relationship between Cd bioaccessibility using different in vitro assays and Cd bioavailability in contaminated soils. Juhasz et al. (2010) correlated Cd bioavailability with Cd bioaccessibility based on different assays, however, only 7 soils were used in that study. Therefore, additional soils are needed to verify their ability to predict Cd bioavailability in contaminated soils.

In this study, 12 Cd-contaminated soils were collected from different locations and contamination sources in China. Four assays including UBM, SBRC, IVG, and PBET were used to determine Cd bioaccessibility in soils. In addition, a 10-day steady state dosing exposure was used to measure Cd bioavailability using a mouse model, with the Cd concentrations in the kidneys, liver, femur, or liver plus kidneys being used as biomarkers. The objectives of this study were to: 1) measure Cd relative bioavailability (RBA) in contaminated soils using a mouse model; 2) determine Cd bioaccessibility in contaminated soils using four in vitro assays; and 3) assess the suitability of in vitro assays to predict Cd bioavailability in contaminated soils by correlating Cd bioaccessibility with Cd-RBA in contaminated soils. This study may help to develop Cd bioaccessibility method to predict Cd bioavailability during risk assessment of Cd-contaminated soils.

2. Materials and methods

2.1. Contaminated soils

Twelve Cd-contaminated soils were collected from different sites, which were impacted by farming, mining, smelting and residential activities in 5 provinces of China (Table 1). Air-dried soils were sieved to <250 μm particle size to obtain the fraction that is easily ingested by hand-to-mouth activities. Concentrated HNO_3 and 30% H_2O_2 were used to digest soils to obtain total Cd, Ca, Fe, Zn, and P concentrations following USEPA Method 3050B. Soil pH was determined in water extracts (1:5 soil: solution) after 2 h of shaking. Total organic carbon (TOC) content was determined as loss on ignition at 900 °C using an element analyzer (vario TOC select, Elementar, Germany) after removing carbonate carbon with HCl. Amorphous Fe, Al, and Mn oxides (Fe_{AM}, Al_{AM},and Mn_{AM}) were extracted using acid ammonium oxalate (McKeague and Day 1966). A laser diffractometer (Mastersizer 2000, Malvern, UK) was used to obtain clay content. Inductively coupled plasma mass spectrometry was used to measure Cd concentration in extracts (ICP–MS, NexIONTM300X, Perkin Elmer, USA), while Fe, Al, Mn, and Ca were quantified using inductively coupled plasma optical emission spectrometry (ICP–OES, Optima 5300, Perkin-Elmer, USA). The optimizing procedures and operating parameters were provided in supporting information (Tables S1 and S2). Soil reference material D061-540 from Environmental Resource Associates was included for QA/QC. The recovery for Cd, Fe, Ca, Zn, and P in the reference material was 97.6 ± 5.1, 102.3 ± 4.6, 96.9 ± 5.5, 110 ± 4.8, and 104.3 ± 8.7% ($n = 3$).

2.2. Cadmium relative bioavailability in soils

Female Balb/C mice weighing 18–22 g were used to determine Cd relative bioavailability (RBA) in contaminated soils. Animal care followed the standard procedures of Nanjing University. Mice were housed in metabolic cages with 12/12 light/dark cycles, with rodent diet and Milli-Q water being supplied ad libitum. After acclimation for 7 days, mice were randomly assigned to metabolic cages with one mouse per cage and three mice per group. Soils were incorporated into mouse basal diet at 1:50 mass ratio in soil-amended diet with Cd concentrations of 0.06–5.92 mg kg^{-1} dry weight (dw). Similarly, $CdCl_2$-amended diet with 0.5–5.0 mg kg^{-1} Cd was prepared. All diets were molded into pellets and freeze-dried.

After fasting overnight, mice were weighed and fed with ~4 g of prepared diet daily over a 10-day period. Mice fed with basal diet were used as control. Dosed concentrations at 0–800 μg Cd Kg BW day^{-1} ($CdCl_2$) were used to establish a dose–response curve for Cd. For soil-amended food, Cd exposure doses were 11–1082 μg Cd Kg BW day^{-1}. At the end of 10 days, mice were fasted overnight again, weighed and

Table 1
Properties of soils (<250 μm particle size) used in this study.

ID	Location (province)	Land uses	Cd (mg kg^{-1})	Ca (g kg^{-1})	Fe (g kg^{-1})	Zn (mg kg^{-1})	P (mg kg^{-1})	pH	TOC (%)	Clay (%)	Al_{AM}[a] (g kg^{-1})	Fe_{AM} (g kg^{-1})	Mn_{AM} (mg kg^{-1})
S1	Hunan	Mining	3.00 ± 0.50[b]	7.37 ± 0.20	134.3 ± 1.7	834 ± 84	205 ± 18	2.8	0.64	13.1 ± 0.24	2.82 ± 0.23	45.5 ± 1.6	2.58 ± 0.12
S2	Yunan	Mining	9.59 ± 0.23	6.61 ± 0.42	104.1 ± 6.2	1801 ± 36	336 ± 11	7.8	1.26	13.4 ± 0.05	2.69 ± 0.24	5.10 ± 0.62	8463 ± 451
S3	Jiangsu	Farming	11.1 ± 3.2	14.2 ± 0.32	51.1 ± 0.21	2404 ± 31	834.8 ± 9.2	7.5	2.23	2.91 ± 0.21	0.98 ± 0.05	15.4 ± 0.84	1202 ± 21
S4	Henan	Farming	13.6 ± 1.9	42.8 ± 2.3	25.1 ± 1.6	380 ± 32	290.6 ± 5.8	8.3	4.55	7.64 ± 0.16	1.24 ± 0.08	1.95 ± 0.34	275 ± 18
S5	Jiangsu	Smelting	18.6 ± 1.2	11.1 ± 0.37	51.4 ± 0.79	3101 ± 45	211.5 ± 6.3	6.5	1.47	3.86 ± 0.13	1.92 ± 0.14	9.88 ± 0.57	2437 ± 18
S6	Jiangsu	Smelting	25.6 ± 0.88	2.22 ± 0.12	20.7 ± 0.90	1584 ± 59	433.2 ± 8.3	6.1	2.51	9.66 ± 0.18	0.74 ± 0.05	6.08 ± 0.52	141 ± 4.3
S7	Hunan	Farming	36.1 ± 0.71	4.71 ± 0.14	30.2 ± 0.26	560 ± 91	9246 ± 13	7.2	2.12	7.15 ± 0.46	1.34 ± 0.21	12.7 ± 0.12	349.3 ± 5.8
S8	Henan	Farming	59.7 ± 1.3	16.4 ± 0.01	28.4 ± 0.47	210 ± 91	170.4 ± 4.5	8.3	2.41	8.37 ± 0.03	1.24 ± 0.12	1.76 ± 0.06	330.1 ± 8.2
S9	Shandong	Residential	130.3 ± 7.3	6.59 ± 0.40	21.1 ± 1.1	50.7 ± 7.3	244.5 ± 6.3	7.8	3.14	3.44 ± 0.18	0.87 ± 0.09	4.51 ± 0.75	497.4 ± 5.4
S10	Shandong	Industry	204 ± 13	5.59 ± 0.63	34.3 ± 1.8	349 ± 18	2297 ± 20	7.8	5.26	3.83 ± 0.06	5.88 ± 0.25	12.5 ± 0.41	270.8 ± 2.5
S11	Shandong	Residential	212 ± 3.6	6.46 ± 0.02	29.9 ± 0.06	380 ± 11	13,173 ± 12	7.3	2.69	3.62 ± 0.06	2.17 ± 0.11	8.84 ± 0.13	424.1 ± 3.4
S12	Jiangsu	Smelting	296 ± 21	48.1 ± 1.0	29.3 ± 0.87	44.5 ± 7.6	560.6 ± 4.6	8.9	3.16	3.51 ± 0.31	2.06 ± 0.17	7.94 ± 0.65	251.3 ± 5.3

[a] AM = amorphous.
[b] Values represent mean and standard deviation of triplicates.