

Supplementary Materials

Article

Environmental and health risk of heavy metals in farmland soils of drinking water protection area and contaminated paddy field in Taiwan

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Table S1. Detailed information of the modified BCR sequential extraction procedure

Step	Target phase	Extraction agent and condition
F1	Acid soluble fraction	40 mL acetic acid, 16 h
F2	Reducible fraction	40 mL hydroxyl ammonium chloride, 16 h
F3	Oxidizable fraction	10 mL hydrogen peroxide (30%), digested at 85°C (water bath) for 1 h; 10 mL hydrogen peroxide again, digested at 85°C (water bath) for 1 h; 50 mL of ammonium acetate, pH = 2, 16 h
F4	Residual fraction	Aqua regia digestion

Table S2. The method detection limit, accuracy and precision for heavy metals in various experiments.

	Total concentration			SEP			SBET		PBET	
	MDL (mg/kg)	Accuracy ^a (%)	Precision (RSD, %)	MDL (mg/kg)	Precision (RSD, %)	Recovery ^b (%)	MDL (mg/kg)	Precision (RSD, %)	MDL (mg/kg)	Precision (RSD, %)
As	0.24	105–120	0.24–4.21	-	-	-	-	-	-	-
Hg	0.011	92.4–110	0.24–14.9	-	-	-	-	-	-	-
Cd	0.08	98.3–109	0.61–6.04	0.08	0.01–0.50	80.0–120	-	-	-	-
Cr	0.15	82.1–92.0	0.23–8.92	0.07	0.02–0.84	80.2–120	0.005	0.22–5.00	0.003	0.05–3.15
Cu	0.32	103–106	0.11–10.5	0.05	0.12–1.39	82.2–118	0.015	0.54–6.64	0.007	0.06–3.67
Ni	0.32	98.2–114	0.09–4.57	0.06	0.04–0.36	80.6–120	-	-	-	-
Pb	0.63	91.6–94.2	0.50–4.94	0.08	0.08–0.42	80.8–119	-	-	-	-
Zn	0.33	110–119	0.15–3.06	0.08	0.23–3.51	80.1–12-	0.217	0.16–6.74	0.05	0.23–7.73
Fe	2.93	90.1–92.5	0.41–2.56	-	-	-	-	-	-	-
Mn	13.2	85.3–93.2	0.41–8.36	-	-	-	-	-	-	-

^a The accuracy was analyzed by using solid standard NIST SRM 2710a.; ^b The recovery was calculated by dividing the sum of each fraction of SEP by total concentration.

Table S3. The model parameter of modified synthesis toxicity index (STI).

Model parameter	Parameter definition					
n	The number of heavy metal					
m	The number of heavy metal form					
Ti	The coefficient of the i-th heavy metal toxicity					
Ej	The bioavailability coefficient of the j-th heavy metal form; E _{1 (ACE)} =7, E _{2 (RED)} =5, E _{3 (OXI)} =2, E _{4 (RES)} =0					
Q_i^j	The mass of the i-th heavy metal with j-th combined form, mg/g					
C_Nⁱ	The i-th heavy metal concentration in the natural environment					
Heavy metals	Cd	Cu	Zn	Pb	Ni	Cr
Heavy metal toxicity coefficient (Ti)	30	5	1	5	5	2
Residential land soil background values (mg/kg)	10	300	500	300	150	400

Table S4. Composition and in-vitro parameters for PBET and SBET assays.

Method	Extraction phase	Composition (g/L)	Solid/solution ratio	pH	Extraction time (h)
PBET	Gastric	1.25 g pepsin, 0.5 g sodium malate, 0.5 g sodium citrate, 420 µL lactic acid, 500 µL acetic acid	1:100	2.5	1
	Intestinal	1.75 g bile, 0.5 g pancreatin	1:100	7.0	4
SBET	Gastric	30.03 g glycine	1:100	1.5	1

Table S5. Values of parameters used to calculate the human exposure risk through soil ingestion

Parameter	Symbol	Unit	Value	Reference
Metal concentration in soils	C _{soil}	mg/kg	Cr = 396 (CJ); 55.1 (HH) ^a ; 302 (BZ); 328 (CH) ^a Cu = 66.1 (CJ); 103 (HH) ^a ; 22.7 (BZ); 422 (CH) ^a Zn = 231 (CJ); 439 (HH) ^a ; 74.0 (BZ); 1,010 (CH) ^a	This study
Bioaccessibility (SBET)	BA _{SBET}	Dimensionless	Cr = 0.06 (CJ); 0.03 (HH) ^a ; 0.01 (BZ); 0.06 (CH) ^a Cu = 0.30 (CJ); 0.35 (HH) ^a ; 0.22 (BZ); 0.59 (CH) ^a Zn = 0.46 (CJ); 0.56 (HH) ^a ; 0.05 (BZ); 0.20 (CH) ^a	This study
Bioaccessibility (PBET)	BA _{PBET}	Dimensionless	Cr = 0.03 (CJ); 0.02 (HH) ^a ; 0.13 (BZ); 0.08 (CH) ^a Cu = 0.06 (CJ); 0.18 (HH) ^a ; 0.14 (BZ); 0.52 (CH) ^a Zn = 0.15 (CJ); 0.23 (HH) ^a ; 0.10 (BZ); 0.20 (CH) ^a	This study
Ingestion rate of soils	IR _{oral-soil}	mg/day	100	[1]
Exposure duration	ED	year	25	[2]
Exposure frequency	EF	day/year	350	[1]
Conversion factor	CF	kg/mg	10 ⁻⁶	-
Body weight	BW	kg	61.67	[2]
Lifetime	LT	year	75	[3]
Averaging time	AT	day	ED*350=8,750 (Non-carcinogens) LT*350=26,250 (Carcinogens)	[3]
Oral reference dose	RfD _{oral}	mg/kg/day	Cr = 3.00E-03 Cu = 1.00E-03 Zn = 3.00E-01	IRIS ASTDR IRIS
Oral slope factor	SF _{oral}	1/(mg/kg/day)	Cr = 5.00E-01	CALEPA

^aThe metal concentrations and bioaccessibility of Cr, Cu and Zn in HH as well as in CH are geometric mean.

Table S6. Values of parameters used to calculate the human exposure risk through soil dermal contact.

Parameter	Symbol	Unit	Value	Reference
Metal concentration in soils	C _{soil}	mg/kg	Cr = 396 (CJ); 55.1 (HH) ^a ; 302 (BZ); 328 (CH) ^a Cu = 66.1 (CJ); 103 (HH) ^a ; 22.7 (BZ); 422 (CH) ^a Zn = 231 (CJ); 439 (HH) ^a ; 74.0 (BZ); 1,010 (CH) ^a	This study
Adherence factor	AF	mg-event/cm ²	0.07	[4]
Fraction of chemical absorbed dermally	ABS _d	Dimensionless	Cr = 0.01 Cu = 0.01 Zn = 0.01	SGM system, Taiwan EPA
Conversion factor	CF	kg/mg	10 ⁻⁶	-
Absorbed dose per event	DA _{event}	mg-event/cm ²	Cr = 2.8E-07 (CJ); 3.9E-08 (HH); 2.1E-07 (BZ); 2.3E-07 (CH) Cu = 4.6E-08 (CJ); 7.2E-08 (HH); 1.6E-08 (BZ); 3.0E-07 (CH) Zn = 1.6E-07 (CJ); 3.1E-07 (HH); 5.2E-08 (BZ); 7.1E-07 (CH)	-
Exposure frequency of the event	EV	event/day	1	[2]
Surface area of body	SA	cm ²	17,300	[2]
Exposure duration	ED	year	25	[2]
Exposure frequency	EF	day/year	350	[1]
The ratio between the surface area of upper arms and the body	f _{sa}	Dimensionless	0.2	[5]
Body weight	BW	kg	61.67	[2]
Lifetime	LT	year	75	[3]
Averaging time	AT	day	ED*350=8,750 (Non-carcinogens) LT*350=26,250 (Carcinogens)	[3]
Dermal reference dose	RfD _{dermal}	mg/kg/day	Cr = 6.00E-05 Cu = 1.20E-02 Zn = 6.00E-02	RAIS RAIS RAIS

^aThe metal concentrations and bioaccessibility of Cr, Cu and Zn in HH as well as in CH are geometric mean.

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