Supporting Information

Modeling mass balance of cadmium in paddy soils under long term control scenarios

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1. Sampling and preparation

A sampling campaign was performed in two sampling sites: an urban site in Yuhu district of Xiangtan (112°51′33″ E, 27°49′36″ N) and a rural site located in a village in southeastern Zhuzhou (113°12′7.97″ E, 27°33′50.42″ N). The Cd concentrations in irrigation water, groundwater and surface runoff, were sampled monthly. Simultaneously, soil water content and dry bulk density were determined by cutting ring method and gravimetric method. The irrigation water and groundwater samples were collected and preserved by cooperant famers. Runoff sample collected in guttering around the each plot was directed out into a plastic bucket in an artificial pond. Before each sampling, the water was drained by an electric pump (YT-25B, Youben, Kunshan, China). A total of 72 atmospheric bulk deposition samples were collected monthly using a time-integrating passive sampler (Polyvinyl chloride cylinders of 50 cm in height and 20 cm in diameter) at each site. Ahead of sampling, the samplers were soaked with 10% HCl solution for 24 h and then rinsed with Milli-Q water (18 MΩ cm^{-1}) for 3 times. Triplicate samplers were kept open at an average height of 1.5 m in the field.

Soils and corresponding rice plant samples were taken from the fields. At maturity stage of rice, soil at the depth of 0-20 cm and rice plants including roots were randomly sampled, and three random subsamples were collected in each plot. Soil samples were air-dried at room temperature, and were treated to remove stones and plant debris, then, were pulverized by an agate mortar. The pulverized samples were ground to pass through 0.149 mm nylon sieve for the determination of total Cd. The rice plant was first washed with tap water to remove adhering soil, and rinsed by deionized water, then separated into roots, straw and grains. The separated plants were kept in an oven at 105 ^{o}C for 30 min and dried in the oven at 60 ^{o}C to constant weight, and were then ground into powder for further analysis.

2. Chemical analysis

The samples of atmospheric deposition were first digested with concentrated HNO_3 and HF using a Microwave-assisted Reaction System according to Guo et al. (2017) (CEM MARS6, CEM Corporation, USA). Digested solutions were then diluted to 25ml with 1% HNO_3 solution. All of them were stored in dark at 4 ^{o}C, and determined within one month. All water samples were prepared according to CMEP (2013, 2014). The concentrations of Cd in atmospheric deposition and water were determined by inductively coupled plasma mass spectrometer (ICP-MS X2, Thermo Fisher, Germany) at Hunan Academy of Agricultural Sciences. To ensure reliability and quality of data, standard reference soil (GBW070011) and fly ash (GBW08401) were purchased from the Center of National Reference Materials of China were employed. Recovery values ranged from 80% to 95%. All observed results were corrected by blank. The relative standard deviations (RSD) were lower than 10%.

For analysis of Cd in fertilizer, lime, soil, rice straw and grain, the prepared samples were digested in digestion system (SH230 Haineng instruments, China). The ground fertilizer, lime, soil samples were digested by digested by HNO_3-HF-$HClO_4$ method CMEP (2005, 2009). The milled plant samples were digested by using HNO_3-$HClO_4$ method according to Lu (2000). The Cd concentrations in fertilizer, lime, soil, rice straw and grain were detected by ICP-MS, respectively. Triplicates were conducted for each treatment. For quality control (QC), the certified reference materials, GBW070011 for soil and GBW10010 for rice were used in the whole analysis process of total and available Cd. The detected values in reference materials were all inside of the certified concentration ranges.

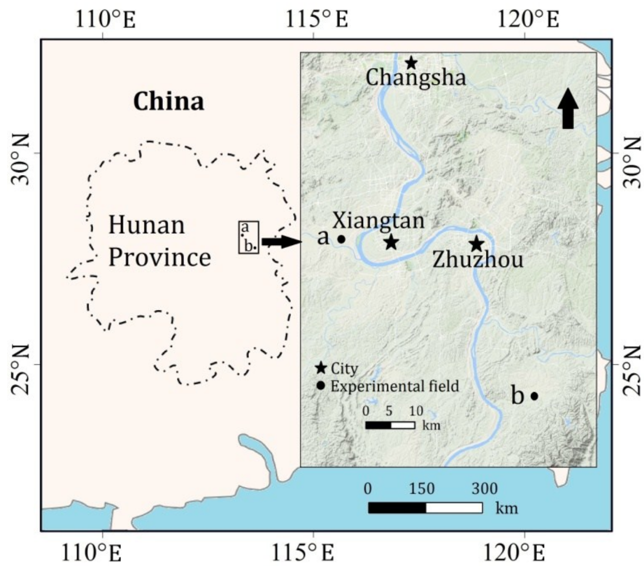

Figure SI-1. Location of two experimental sites in Hunan Province.

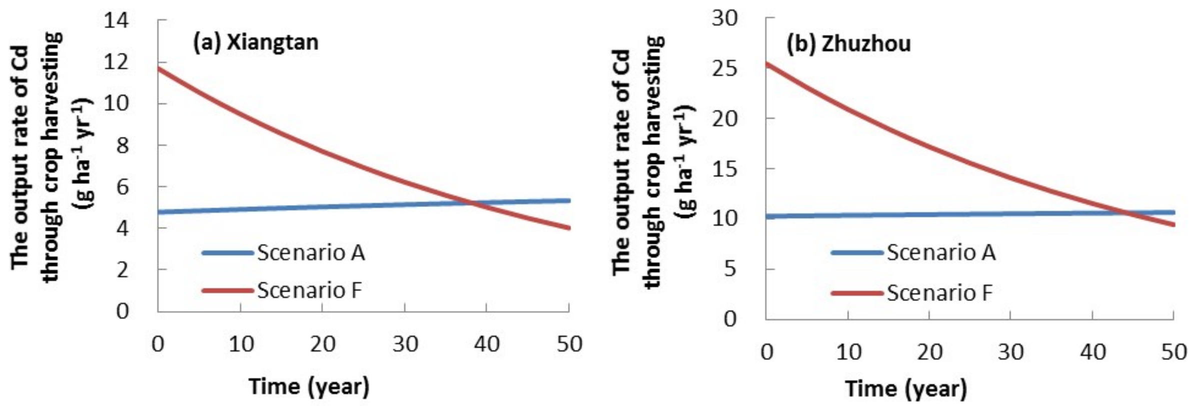

Figure SI-2. Changes of the output rate of Cd through crop harvesting in 50 years of continuous cultivation under default (A) and integrating scenarios (F).

Table SI-1. The average of Cd concentration in input and output materials of experimental fields.

	Units	**Xiangtan**	**Zhuzhou**
Lime	mg kg^{-1}	0.179	0.179
Fertilizer[a]	mg kg^{-1}	0.123	0.323
Irrigation	μg L^{-1}	0.5939	1.018
Ground water	μg L^{-1}	0.0008	0.0015
Runoff	μg L^{-1}	0.3418	0.2630

[a]The compound fertilizer for rice was used as a base fertilizer (N:P:K =16:16:16), applied to the soil at 1133 kg ha^{-1} season^{-1}.

Table SI-2. Calculation of the atmospheric deposition flux of Cd.

Month	Cd concentration (μg L^{-1})		Depth (cm)		Cd flux (g ha^{-1})	
	Xiangtan	Zhuzhou	Xiangtan	Zhuzhou	Xiangtan	Zhuzhou
Apr-15	1.25	0.23	17.09	16.39	2.14	0.38
May-15	1.75	0.33	11.19	17.72	1.96	0.59
Jun-15	1.32	0.61	9.71	7.94	1.28	0.49
Jul-15	0.88	0.74	17.97	3.74	1.59	0.27
Aug-15	1.59	1.71	7.06	8.80	1.12	1.50
Sep-15	1.43	3.47	8.65	7.84	1.23	2.72
Oct-15	0.27	5.99	8.48	8.37	0.23	5.01
Nov-15	1.36	4.33	8.05	9.80	1.10	4.24
Dec-15	2.65	7.33	2.98	5.06	0.79	3.71
Jan-16	0.96	3.78	4.79	5.81	0.46	2.20
Feb-16	0.54	1.82	4.68	4.57	0.25	0.83
Mar-16	0.45	0.80	26.78	21.31	1.20	1.71
Total	—	—	127.43	117.35	**13.35**	**23.66**

Table SI-3. The total volumes of annual irrigation and precipitation for calculations. The data are all from water resources bulletin of Hunan Province.

Year	Irrigation (mm)		Precipitation (mm)	
	Xiangtan	Zhuzhou	Xiangtan	Zhuzhou
2009	855	837	1261	1296
2011	760	714	1527	1859
2013	868	870	1498	1625
2015	862	855	1457	1810
Mean	836	819	1436	1647
Standard deviation	51	71	120	255

Table SI-4. The total volumes of annual evapotranspiration and leaching for calculations. The values of evaporation and crop coefficients from monitoring result by (Zou et al., 2002).

	Xiangtan	Zhuzhou
Evaporation (mm)	1055	941
Crop coefficients	1.3350	1.3005
Evapotranspiration (mm)	1408	1224
Run off (mm)	613	990
Leaching (mm)	251	251

Table SI-5. The water balance in the experimental paddy fields

	Xiangtan	Zhuzhou
Input (mm)		
Irrigation	836	819
Precipitation	1436	1647
Total	2272	2466
Output (mm)		
Surface runoff	613	990
Evapotranspiration	1408	1224
Leaching	251	251
Total	2272	2465

Table SI-6. Statistic characteristics and distribution of variations under two scenarios in the Monte Carlo simulation.

Parameter	Xiangtan		Zhuzhou		Distribution
	Scenario A	Scenario F	Scenario A	Scenario F	
ϑ (m^3 m^{-3})	0.27±0.02	0.27±0.02	0.25±0.02	0.25±0.02	Normal
ρ (kg m^{-3})	1.02±0.13	1.02±0.13	1.06±0.24	1.06±0.24	Normal
K_d (m^3 kg^{-1})	163.29±81.00	163.29±81.00	163.29±81.00	163.29±81.00	Log-normal
PUF	2.51±1.23	2.51±1.23	2.41±1.54	2.41±1.54	Log-normal
Y (t ha^{-1} yr^{-1})	14.5±1.56	28.5±4.10	15.0±1.56	29.8±5.11	Normal
v (cm h^{-1})	0.0029±0.00121	0.0029±0.00121	0.0029±0.00121	0.0029±0.00121	Normal

Table SI-7. Calculated results of input parameters of test fields under six remediation scenarios.

Parameters	Scenarios A	Scenarios B	Scenarios C	Scenarios D	Scenarios E	Scenarios F
Xiangtan						
i (10^{-3} mg kg^{-1} yr^{-1})	8.091	8.091	6.171	1.547	8.355	-0.622
k_u (10^{-3} yr^{-1})	7.027	28.649	7.027	7.027	4.216	17.189
k_l (10^{-3} yr^{-1})	2.036	2.036	2.036	2.036	2.544	2.544
Zhuzhou						
i (10^{-3} mg kg^{-1} yr^{-1})	14.318	14.318	10.918	3.138	14.572	-0.620
k_u (10^{-3} yr^{-1})	6.937	27.677	6.937	6.937	4.162	16.606
k_l (10^{-3} yr^{-1})	1.841	1.841	1.841	1.841	2.301	2.544

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