

Supplementary Materials

Figure 1 showed the contents of metal(loid)s in three surface waters and their maximum allowable concentrations (MAC) used for agricultural irrigating. Sample SY-1 (surface water sampling site were abbreviated by "SY") was collected from the reservoir which is located in the upstream of the mining area. Site SY-2 is located in the Ji Changling reservoir which is close to the downstream of the mining area. Site SY-3 is also located in the downstream of the mining area but is farther from the mine zone, which is close to the residential areas. The surface water of Jichangling reservoir has been polluted by arsenic, and also showed higher Zn, Cu, Pb concentrations than the ones of the other reservoir.

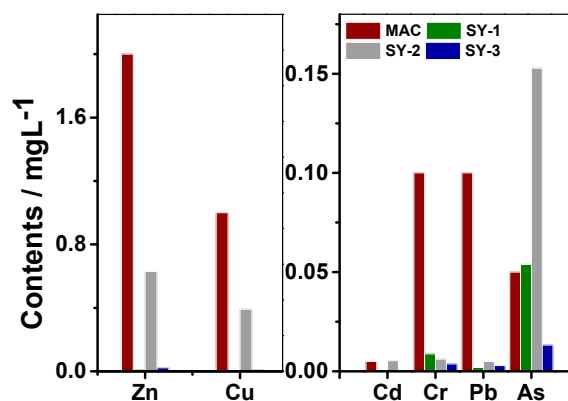


Figure S1. The contents of metal(loid)s and in three surface waters and their maximum allowable concentrations (MAC) used for agricultural irrigating.

Table S1. Sequential extraction methods for metal(loid)s in different depth soils from the study area

Step	Fractions	Extract composition	pH	Notes
F ₁	Water soluble	25 mL ultrapure water	pH=8.0 ± 0.2	30 min ultrasound (40 KHz, 25 ± 5°C), rinse with ultrapure H ₂ O.
F ₂	Exchangeable	25 mL 1.0 mol/L MgCl ₂ ·6H ₂ O	pH=7.0 ± 0.2	30 min ultrasound (40 KHz, 25 ± 5°C), rinse with ultrapure H ₂ O.
F ₃	Carbonate-bound	25 mL 1.0 mol/L CH ₃ COONa·3H ₂ O	pH=5.0 ± 0.2	60 min ultrasound (40 KHz, 25 ± 5°C), Rinse with ultrapure H ₂ O.
F ₄	Humic acid-bound	50 mL 0.1 mol/L Na ₄ PO ₇ ·10H ₂ O	pH=10.0 ± 0.2	40 min ultrasound (40 KHz, 25 ± 5°C), rinse with ultrapure H ₂ O.
F ₅	Fe and Mn oxide-bound	50 mL 0.25 mol/L HONH ₃ Cl-HCl		1 h ultrasound (40 KHz, 25 ± 5°C), rinse with ultrapure H ₂ O.
F ₆	Refractory organic matter-bound	3 mL HNO ₃ +5 mL 30% H ₂ O ₂	pH=2.0±0.2	1.5 h bath (83 °C, stirred every 10 min), another 1.0 h bath with 3 mL 30% H ₂ O ₂ (83 °C, stirred every 10 min), rinse with ultrapure H ₂ O.
F ₇	Residual	5 mL mixture of 37%HCl -70%HClO ₄ -70%HNO ₃ (1:1:1)/5 mL 40%HF		Digested at 105 °C for 3h.

Table S2. Concentrations and enrichment factors (*EFs*) of metal(loid)s in top soils from the study area

Sample	Cr		Ag		B		Bi		Co		Mo	
	Concentration (mg/kg)	<i>EF</i>	Concentration (mg/kg)	<i>EF</i>	Concentration (mg/kg)	<i>EF</i>	Concentration (mg/kg)	<i>EF</i>	Concentration (mg/kg)	<i>EF</i>	Concentration (mg/kg)	<i>EF</i>
TY-1	43.7 ± 0.8	0.69	0.454 ± 0.003	3.34	200.0 ± 1.2	7.30	13.10 ± 0.07	19.30	11.7 ± 0.3	1.33	1.29 ± 0.03	0.13
TY-2	8.1 ± 0.2	0.27	0.072 ± 0.004	1.13	22.0 ± 0.4	1.71	0.53 ± 0.01	1.67	5.0 ± 0.2	1.21	1.13 ± 0.02	0.25
TY-3	44.9 ± 0.3	0.52	0.523 ± 0.005	2.82	200.0 ± 0.9	5.34	8.47 ± 0.08	9.14	20.2 ± 0.5	1.68	1.21 ± 0.04	0.09
TY-4	44.0 ± 0.2	0.52	0.250 ± 0.004	1.38	200.0 ± 0.8	5.49	2.66 ± 0.05	2.95	10.0 ± 0.2	0.85	0.89 ± 0.03	0.07
TY-5	46.6 ± 0.8	0.61	0.194 ± 0.003	1.18	91.6 ± 0.6	2.76	1.68 ± 0.04	2.04	10.5 ± 0.3	0.98	1.07 ± 0.03	0.09
TY-6	42.4 ± 0.3	0.64	0.291 ± 0.002	2.07	53.8 ± 0.3	1.89	1.33 ± 0.04	1.89	7.7 ± 0.2	0.84	0.87 ± 0.02	0.09
TY-7	47.3 ± 0.4	0.62	0.394 ± 0.002	2.40	79.1 ± 0.2	2.39	2.66 ± 0.04	3.24	13.2 ± 0.6	1.24	1.11 ± 0.02	0.09
TY-8	37.4 ± 0.3	0.62	0.150 ± 0.002	1.16	89.5 ± 0.6	3.42	0.25 ± 0.02	0.39	11.5 ± 0.1	1.37	1.48 ± 0.04	0.16
TY-9	16.9 ± 0.1	0.64	0.095 ± 0.005	1.69	11.5 ± 0.1	1.01	1.12 ± 0.01	3.99	4.3 ± 0.3	1.18	3.80 ± 0.08	0.95
TY-10	18.6 ± 0.1	0.19	0.162 ± 0.002	0.79	9.9 ± 0.3	0.24	0.47 ± 0.01	0.46	14.3 ± 0.3	1.07	1.89 ± 0.04	0.13
TY-11	49.7 ± 0.2	0.40	0.876 ± 0.006	3.30	54.3 ± 0.4	1.01	2.61 ± 0.06	1.96	14.5 ± 0.4	0.84	1.91 ± 0.02	0.10
Max	49.7	0.69	0.876	3.34	200	7.30	13.10	19.30	20.2	1.68	3.8	0.95
Min	8.1	0.19	0.072	0.79	9.9	0.24	0.25	0.39	4.3	0.84	0.87	0.07
Mean	36.3	0.52	0.314	1.93	91.9	2.96	3.17	4.27	11.17	1.15	1.51	0.20
SD	14.5	0.16	0.237	0.91	74.9	2.22	4.00	5.52	4.54	0.26	0.83	0.25
BV ^a	50.5		0.108		21.8		0.54		7.0		7.7	
MAC ^b	300		---		---		---		---		---	

BV: background value; MAC: maximum allowable concentration.

^a background values of elements in the soils of Guangdong Province (CNEMC, China National Environmental Monitoring Center, 1990 [27]),

^b The maximum allowable concentrations of contaminants in Chinese soils (EPAC, Environmental protection Administration of China, 2008 [41]).

Table S2. (Continued) Concentrations and enrichment factors (EFs) of metal(loid)s and phosphorus in top soils from the study area.

Sample	Sb		Ti		V		W		Sn		P
	Concentration (mg/kg)	EF	Concentration (mg/kg)	EF	Concentration (mg/kg)	EF	Concentration (mg/kg)	EF	Concentration (mg/kg)	EF	Concentration (mg/kg)
TY-1	1.41 ± 0.04	2.08	4790.1 ± 7.6	1.31	60.5 ± 0.9	0.74	130.0 ± 0.5	32.83	35.9 ± 0.6	4.92	942.1 ± 1.0
TY-2	0.60 ± 0.06	1.89	1708.2 ± 5.3	1.00	16.9 ± 0.3	0.44	1.8 ± 0.05	0.96	5.8 ± 0.3	1.70	199.8 ± 1.5
TY-3	1.46 ± 0.03	1.57	4979.0 ± 6.2	1.00	64.0 ± 0.8	0.57	53.8 ± 0.6	9.95	34.6 ± 0.5	3.47	1430.1 ± 1.5
TY-4	1.69 ± 0.05	1.87	4850.2 ± 3.2	1.00	60.2 ± 0.4	0.55	7.7 ± 0.4	1.46	28.9 ± 0.4	2.98	772.3 ± 1.6
TY-5	1.08 ± 0.01	1.31	4419.0 ± 4.0	1.00	69.8 ± 0.2	0.70	10.7 ± 0.3	2.23	16.9 ± 0.3	1.91	909.4 ± 1.4
TY-6	0.92 ± 0.06	1.30	3776.8 ± 3.2	1.00	53.2 ± 0.5	0.63	6.3 ± 0.4	1.54	23.1 ± 0.2	3.06	1793.9 ± 1.5
TY-7	1.31 ± 0.03	1.60	4402.6 ± 5.6	1.00	72.5 ± 0.6	0.73	20.4 ± 0.5	4.27	19.2 ± 0.8	2.18	1451.2 ± 1.3
TY-8	1.21 ± 0.03	1.87	3479.5 ± 5.6	1.00	47.3 ± 0.6	0.60	2.4 ± 0.2	0.64	3.3 ± 0.2	0.47	464.8 ± 1.3
TY-9	1.04 ± 0.02	3.70	1507.8 ± 6.7	1.00	19.2 ± 0.3	0.57	2.6 ± 0.2	1.59	9.7 ± 0.2	3.22	374.3 ± 0.9
TY-10	1.54 ± 0.04	1.50	5518.2 ± 3.6	1.00	84.7 ± 0.6	0.68	2.0 ± 0.1	0.34	6.9 ± 0.2	0.63	479.6 ± 1.2
TY-11	1.61 ± 0.03	1.21	7135.5 ± 8.9	1.00	113.4 ± 0.5	0.71	8.0 ± 0.4	1.04	20.7 ± 0.4	1.45	1496.9 ± 1.0
Max	1.69	3.70	7135.5	1.31	113.4	0.74	130	32.83	35.9	4.92	1793.9
Min	0.60	1.21	1507.8	1.00	16.9	0.44	1.79	0.34	3.3	0.47	199.8
Mean	1.26	1.81	4233.3	1.03	60.1	0.63	22.3	5.17	18.6	2.36	937.7
SD	0.33	0.69	1611.3	0.09	27.3	0.09	38.7	9.57	11.4	1.32	511.3
BV ^a	0.54		2900		65.3		3.15		5.8		---
MAC ^b	---		---		---		---		---		---

BV: background value; MAC: maximum allowable concentration.

^a background values of elements in the soils of Guangdong Province (CNEMC, China National Environmental Monitoring Center, 1990 [27]),

^b The maximum allowable concentrations of contaminants in Chinese soils (EPAC, Environmental protection Administration of China, 2008 [41]).

Table S3. Major constituents (mg/kg) of the common chemical fertilizers and pesticides from the study area.

Type	Description	Unit	As	Cu	Pb	Zn	Cd	Ni	Cr	Ca	Mn	K	Mg	N	P
Chemical fertilizers	Kalium chloratum	mg/kg	<0.5	1.5	<0.1	2.2	0.6	8.0	1.3	0.8	2.1	2.7×10 ⁵	505	3.2	2.7
	Carbamide	mg/kg	<0.5	<1.0	<0.1	<0.5	0.04	2.4	<1.0	0.4	1.2	302.5	5.3	4.3×10 ⁵	1.4
	Superphosphate	mg/kg	2.0	85.8	3.3	58.3	2.6	25.8	10.5	7.5	315	2.2×10 ³	1.5×10 ⁴	19.5	6.0×10 ⁴
Pesticides	Buprofezin	mg/kg	1.0	13.2	<0.1	40.5	1.0	32.0	1.5	8.6	95	1.5×10 ³	20.9	2.4×10 ³	401.1
	Yeshuangqing	mg/kg	1.0	2.6	<0.1	10.5	1.2	2.1	2.6	0.2	103.1	3.1×10 ³	173.3	1.3×10 ⁴	762.7
	Bishuangling	mg/kg	0.6	8.4	<0.1	14.5	1.6	14.5	<0.5	2.3×10 ⁵	17.7	271.6	311.0	2.9×10 ⁴	1.6×10 ²
	Lorsban	mg/kg	<0.5	2.1	<0.1	1.0	0.1	4.2	<0.5	400	0.6	0.7	12.4	8.7×10 ³	10.3×10 ³
	Suihua 203 emulsion	mg/L	<0.5	<1.0	<0.1	6.0	0.2	3.1	2.2	0.04	0.5	ND	8.9	213.7	159.5
	Acephate	mg/L	<0.5	<1.0	<0.1	<0.5	0.4	3.6	1.0	0.006	0.5	ND	0.7	2.8×10 ³	4.8×10 ³
	Hipro sulfur phosphorus	mg/L	<0.5	<1.0	<0.1	3.1	0.04	0.1	1.0	0.08	0.1	9.4	9.4	7.5×10 ³	27.6
	Emamectin benzoate	mg/L	<0.5	<1.0	<0.1	1.6	<0.01	<0.05	1.0	0.09	0.2	60.5	48.4	3.2×10 ³	12.4

ND-not detected.

Table S4. Total concentrations of trace elements in three different soil layers.

Element	Soil layer	TY-1	TY-2	TY-3	TY-4	TY-5	TY-6	TY-7
As	A horizon	219.8	10.8	181.8	68.5	52.4	43.8	57.8
	B horizon	271.2	9.7	216.2	298	87.5	218.6	40.9
	C horizon	183.6	10	320.3	300.2	151.2	176	17.8
Cd	A horizon	0.149	0.069	0.171	0.209	0.193	0.348	0.333
	B horizon	0.324	0.12	0.392	0.18	0.109	0.386	0.087
	C horizon	0.242	0.07	0.27	0.17	0.151	0.252	0.168
Cu	A horizon	88.7	7.4	80.9	39.3	28.8	27.7	34.6
	B horizon	191.1	12.3	112.5	158.6	47.6	93.7	33.5
	C horizon	157.3	5.6	161.2	171.3	74.5	89.5	16.8
Ni	A horizon	13.6	5.6	15.5	13.8	15.8	13.7	16.8
	B horizon	21.2	5.2	23.7	35.2	21.8	36	27.8
	C horizon	17.1	5.3	28.6	37.6	31.6	34.8	16.9
Pb	A horizon	133.5	32.3	99	75.8	76.2	136.8	118.1
	B horizon	159.8	33.1	97.8	163	99.8	212.3	87.8
	C horizon	157.6	30.5	112	203.5	186.7	207.4	49.7
Zn	A horizon	150.7	59.6	131.2	116.4	97.1	137.3	156.4
	B horizon	211	58.7	218.9	262.3	135.2	364.3	108.9
	C horizon	215	61.2	251.2	262.1	191.3	363.5	90.1
Cr	A horizon	43.7	8.1	44.9	44	46.6	42.4	47.3
	B horizon	39.7	8.2	32.4	32.5	34.6	36.9	35.9
	C horizon	35.2	7.8	36.8	33.5	35.7	35.8	35.4
Ag	A horizon	0.454	0.072	0.523	0.25	0.194	0.291	0.394
	B horizon	0.432	0.083	0.362	0.261	0.147	0.488	0.138
	C horizon	0.362	0.062	0.522	0.29	0.197	0.412	0.089
B	A horizon	200	22	200	200	91.6	53.8	79.1
	B horizon	198	28	198	198	73	92.7	54
	C horizon	197	17	197	197	103	102.3	51.7
Bi	A horizon	13.1	0.53	8.47	2.66	1.68	1.33	2.66
	B horizon	7.9	0.48	6.21	6.62	3.51	3.36	1.39
	C horizon	7.6	0.23	6.79	6.65	3.67	2.97	1.14
Co	A horizon	11.7	5	20.2	10	10.5	7.7	13.2
	B horizon	6.8	4.8	11.3	12.3	14.5	5.9	14.5
	C horizon	5.8	5.1	11.2	11.4	13.8	6.7	12.2

Table S4 (Continued). Total concentrations of trace elements in three different soil layers

Element	Soil layer	TY-1	TY-2	TY-3	TY-4	TY-5	TY-6	TY-7
Mo	A horizon	1.29	1.13	1.21	0.89	1.07	0.87	1.11
	B horizon	3.45	0.83	2.19	4.08	2.02	3.26	3.28
	C horizon	2.36	0.98	2.68	4.48	2.23	3.87	3.37
Sb	A horizon	1.41	0.601	1.46	1.69	1.08	0.915	1.31
	B horizon	1.74	0.56	2.15	3.18	2.46	2.49	0.82
	C horizon	1.36	0.52	2.53	3.22	3.02	2.54	0.8
Ti	B horizon	4790.1	1708.2	4979	4850.2	4419	3776.8	4402.6
	C horizon	4789.2	1709.3	5672.4	4398.7	5256	5897	5120
	A horizon	5670.8	1880.5	5240	5512.5	5345.2	5643	2672
V	B horizon	60.5	16.9	64	60.2	69.8	53.2	72.5
	C horizon	81.6	16.5	77.8	118.3	86.2	134.6	123.7
	A horizon	79.8	16.7	94.6	119.6	104.7	129	43.8
W	B horizon	13	1.79	53.8	7.69	10.7	6.3	20.4
	C horizon	27.8	1.76	13.8	13.4	7.8	5.9	4.8
	A horizon	25.6	1.65	14.5	12.9	8.2	6.2	3.9
Sn	B horizon	35.9	5.8	34.6	28.9	16.9	23.1	19.2
	C horizon	35.2	3	38.4	28.8	18.7	17.9	14.2
	A horizon	38.6	2.8	34.8	34.6	19.2	18.2	5.6