Short Communication

Thallium, Arsenic, and Mercury Contamination of Soil near the World's Largest and Longest-Operating Tungsten Mine

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Abstract

Little is known about soil thallium contamination near tungsten (W) mines. This study investigated thallium, arsenic, and mercury contents and enrichment in agricultural soils near the world's largest and longest-operating W mine in China. Results show that the long-term W mining significantly elevated Tl from 0.77 to 1.61 $mg \cdot kg^{-1}$ and As from 7.54 to 22.64 $mg \cdot kg^{-1}$, with enrichment factors of 2.0 (1.4 to 3.7) and 2.9 (1.5 to 7.2), respectively. Hg contents were similar at the contaminated site (0.16 $mg \cdot kg^{-1}$) and control site (0.19 $mg \cdot kg^{-1}$), but were two to three times higher than the soil background content of Jianxi province. Thus, Hg contamination in the soil probably was mainly caused by coal and petrol burning instead of W mining.

Keywords: thallium, arsenic, mercury, soil, tungsten, mine

Introduction

Only limited studies have investigated the effects of W mining and smelting on contamination of nearby soils [1-4]. On the other hand, Tl contamination in the soils around W mines has not been studied previously, whereas Tl contamination in soils poses a significant threat to organisms due to its high toxicity and ready assimilation [5, 6].

China was the world's largest W producer and consumer. In 2010, world W mine production was 61,000 t, of which 52,000 t was from China. Ganzhou, in southern Jiangxi province, the birth place of the Chinese W industry and the "Tungsten capital of the world," is extremely rich in W. It has been 100 years since tungsten was discovered in Xihuashan mine in 1907 in Dayu county, Ganzhou.

The objectives of the present study are to determine the As, Hg, and Tl contents in the agricultural soil in the vicinity of the world's largest and longest-operating tungsten mine, and to assess their contamination in the soil.

Materials and Methods

Study Area

The study site is situated in Dayu county in southern Jiangxi province of southern China. It is characterized by a subtropical monsoon climate, with average annual precipitation and temperature of 1591.5 mm and 18.5ºC. Major crops are paddy rice and maize. There are three major tungsten mines in the county: Xihuashan, Dangping, and Piaotang, among which Xihuashan is the first tungsten mine operated in China (Fig. 1). The quartz-bearing veins in an upper crustal Jurassic pluton in Dayu County are a

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typical wolframite-quartz vein deposit. These veins are rich in W, coupled with Sn, Mo, Be, Bi, Cu, Pb, and Zn, etc. Local farmers usually irrigate cultivated fields with river water originating from the W mining area.

Soil Sampling and Analysis

Topsoil samples (0 to 20 cm depth) were collected at three sites: Fujiang (P1), Qinglong (P2), and Jicun (P3) (Fig. 2). Site P1 is located downstream of Xihuanshan Mine, while P2 is downstream of Piaotang Mine. P3 (control site) is located south of the Zhangjiang River across the W mines, and is considered not to be impacted by W mining activity. Ten topsoil samples (about 2 kg) were collected at each site and then transferred to plastic bags. The samples were air-dried in lab, slightly crushed, passed through 2 mm sieve, and stored in glass bottles.

The pH value of each soil sample was analyzed in a 1:10 solid/liquid ratio suspension using a combination pH electrode (Orion, USA). The organic matter concentration was measured by weight loss on ignition to 400ºC [7]. Carbonate content was measured by the manometric method following the addition of dilute HCl to dissolve carbonates [8]. Grain size was determined by an LS 230 laser diffraction particle analyzer (Beckman Coulter), and clay content of less than 2 μm in particle size was calculated.

Portions of the soil samples were digested with HNO_3-HF-$HClO_4$ [9]. The Al, Fe, and Mn in the extracts were measured with ICP-AES (IRIS Intrepid II, Thermo Electron), while Tl was measured with ICP MS (X Series II, Thermo Electron).

Portions of the soil samples were digested with aqua regia [10]. The Hg in the extracts was measured by cold vapor atomic fluorescence spectroscopy (XGY-1011), while As in the extracts was measured using hydride generation atomic fluorescence spectrometry (XGY-1011).

Results and Discussion

General Properties of Soils

Table 1 summarizes levels of some mineral matrix elements, OM, and carbonate, particle distribution, and pH. The organic matter content varied between 2.76% and 6.26%. The carbonate content ranged from 2.94 to 5.98 $g \cdot kg^{-1}$. The soil samples were generally characterized with acidic pH, in the range of 5.09 to 6.28. In general, soil texture was sandy loam, with 1.37 to 5.26% of clay particle, 19.47 to 41.47% of silt particle, and 53.47 to 79.16 of sand particle. Generally, soil properties such as pH, OM, texture, and carbonate were similar at three sites. In addition, the content of Al in the soil also was similar at three sites.

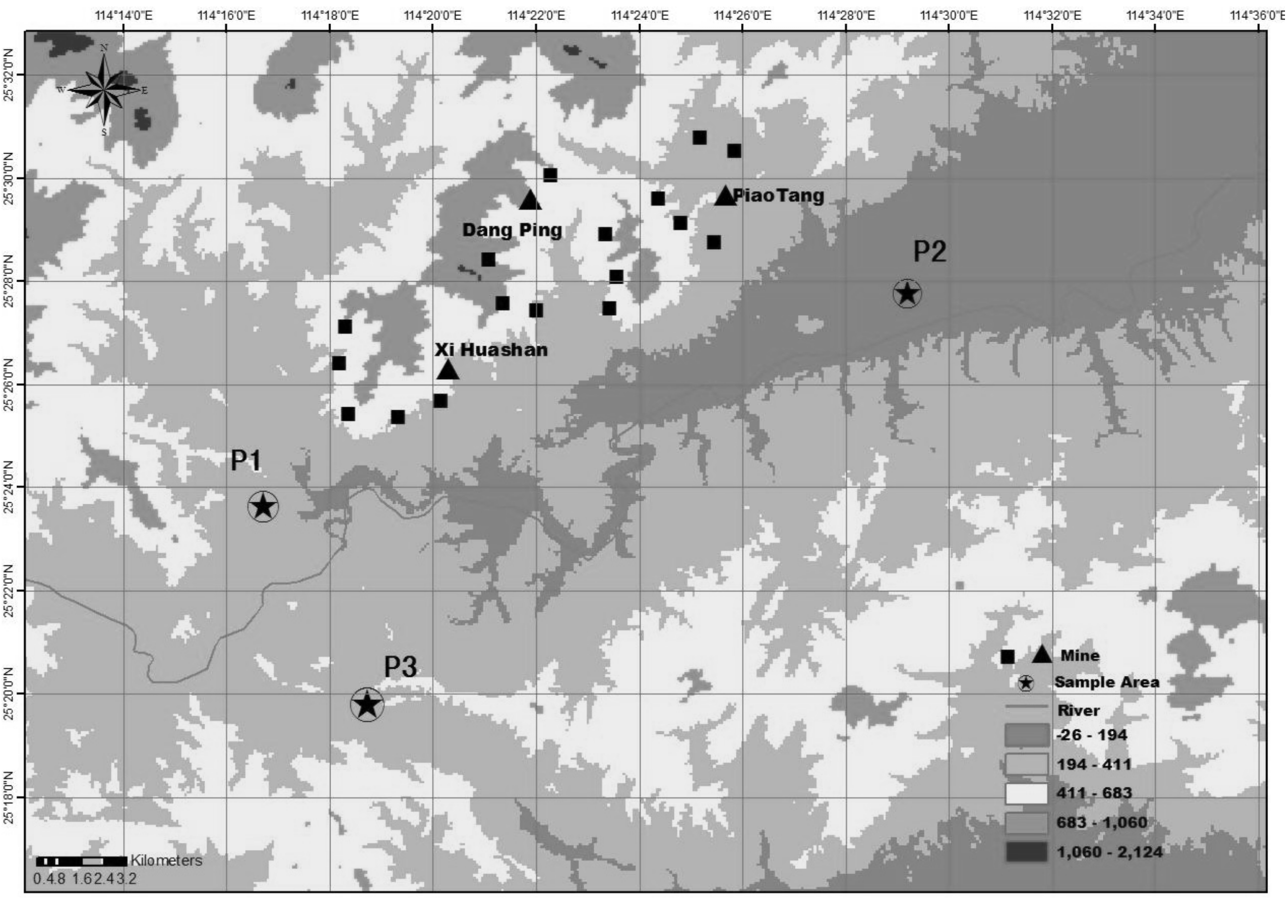

Fig. 1. Schematic graph of W mine locations and soil sampling sites. P1 and P2 sites are considered to be sites contaminated by W mining, while P3 is not considered to be influenced by W mining (control site).

However, contents of Fe and Mn in the soil of sites P1 and P2 were higher than those in the soil of P3, which might be related to W mining.

Contents of As, Hg, and Tl in the Soils

The contents of As, Hg, and Tl also are shown in Table 1. The soil at P1 and P2 contained higher As and Tl than soil at P3 (Table 1, Fig. 2). However, the average content of Hg in the soil at P1 and P2 was similar to that at P3. This indicates that W mining in Dayu County led to As and Tl contamination in the nearby agricultural soil.

The content of As in the soil at P1 and P2 ranged from 11.9 to 55.1 $mg\cdot kg^{-1}$, with an average of 22.6 $mg\cdot kg^{-1}$. On the other hand, the content of As in the soil at P3 ranged from 4.6 to 11.5 $mg\cdot kg^{-1}$, with an average of 7.5 $mg\cdot kg^{-1}$. Thus, the average content of As in the soil at P1 and P2 was much higher than the soil background contents for China (11.2 $mg\cdot kg^{-1}$) and Jiangxi province (14.9 $mg\cdot kg^{-1}$), and that at P3 [12]. In the cultivated soils in southern Poland, arsenic content ranged from 5.0 to 16.5 $mg\cdot kg^{-1}$, with an average of 8.7 [13].

The average content of Tl in the soil at sites P1 and P2 was 1.61 (1.19 to 2.64) $mg\cdot kg^{-1}$, while it was only 0.77 (0.54 to 0.94) $mg\cdot kg^{-1}$ in the soil at P3. The average content of Tl in the soil at P1 and P2 was higher than the soil background contents for China (0.62 $mg\cdot kg^{-1}$) and Jiangxi Province (0.88 $mg\cdot kg^{-1}$), and that at P3. On the other hand, the average content of Tl in the soil at P3 was similar to the soil background contents for China and Jiangxi province.

The average content of Hg in the soil at sites P1 and P2 was 0.16 (0.08 to 0.23) $mg\cdot kg^{-1}$, similar to 0.19 (0.11 to 0.45) $mg\cdot kg^{-1}$ in the soil at P3. In addition, the average contents of Hg in the soils at P1, P2, and P3 were two to three times higher than the soil background contents for China (0.07 $mg\cdot kg^{-1}$), the world (0.06 $mg\cdot kg^{-1}$), and Jiangxi (0.08 $mg\cdot kg^{-1}$). The W veins in Dayu County contain low Hg, so W mining may not be a major anthropogenic source of Hg in the soils. Therefore, anthropogenic sources in the soil of Dayu County may be local atmospheric input. This result is similar to that observed by Doszke and Kowalski [14], indicating that Hg content in the floodplain soils collected below a city (Poznań) was higher than that above of the city, due to atmospheric deposition.

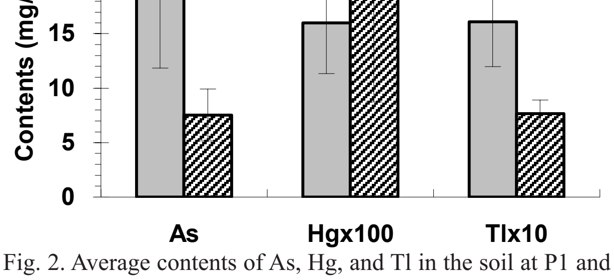

Fig. 2. Average contents of As, Hg, and Tl in the soil at P1 and P2 sites and in the soil at P3 site (control site).

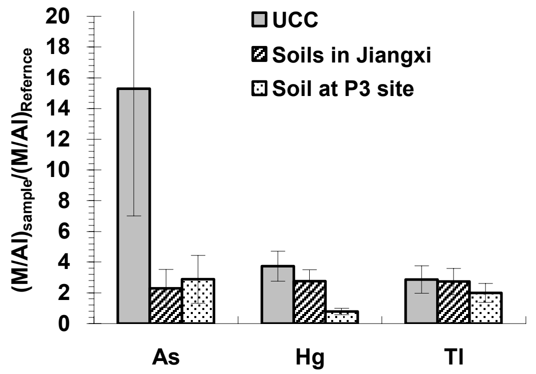

Fig. 3. Enrichment factors (EFs) of As, Hg, and Tl in the soil at sites P1 and P2 , relative to upper continental crust (UCC), the soils in Jiangxi, and the soil at P3 (control site).

Enrichment of As, Hg, and Tl in Soils

Enrichment factors (EF) relative to the elemental background contents were calculated to evaluate the effects of human activities by the following equation:

$$EF=([M]/[Al])_{Sample}/([M]/[Al])_{Reference} \quad (1)$$

...where $([M]/[Al])_{Sample}$ is the ratio of metal content to Al content in the soil samples at P1 and P2, and $([M]/[Al])_{Reference}$ is the average ratio of M content to Al content in the reference materials. The reference materials in this study include upper continental crust (UCC), the soils of Jiangxi Province, and the soil at site P3 (control). EFs are shown in Fig. 3.

Relative to UCC, the average EFs of As, Hg, and Tl in the soil at P1 and P2 were 15.3 (8.0 to 38.3), 3.7 (2.2 to 5.4), and 2.9 (2.0 to 5.4), respectively. Relative to the soils of Jiangxi Province, the average EFs of As, Hg, and Tl in the soil at P1 and P2 were 2.3 (1.2 to 5.7), 2.8 (1.6 to 4.0), and 2.7 (1.9 to 5.1), respectively. However, relative to the soil at P3 (control site), the average EFs of As, Hg, and Tl were 2.9 (1.5 to 7.2), 0.8 (0.5 to 1.1), and 2.0 (1.4 to 3.7) in the soil at P1 and P2, respectively. The results show that the enrichment of As, Hg, and Tl in the soil, caused by W mining activity, can be identified by using local soil background content as a reference.

Conclusions

W mining in Dayu County significantly elevated As and Tl contents, but not Hg content in the agricultural soils near the W mines. The average contents of As and Tl in the soil impacted by W mining were 22.6 and 1.61 $mg\cdot kg^{-1}$, respectively, while they were 7.5 and 0.77 $mg\cdot kg^{-1}$ in the soil unaffected by W mining. The EF relative to the soil not-impacted by W mining ranged from 1.5 to 7.2 for As and 1.4 to 3.7 for Tl, with an average of 2.9 and 2.0, respectively. Previous studies reported contamination by As, Sb, Bi, Cd, Cu, Pb, and Zn in soils around W mines, while this study further showed Tl contamination in the soil around the W

Table 1. Physicochemical properties and elemental contents in the soils at Fujiang (P1), Qinglong (P2), and Jicun (P3) sites in Dayu County.

Sample	pH	OM	Carb	Clay	Silt	Sand	As	Hg	Tl	Mn	Fe	Al
		%	g/kg	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	%	%
Soil contaminated by W mining (P1 and P2 sites)												
1	6.09	3.56	3.96	1.37	19.47	79.16	16.02	0.16	1.27	381.8	2.01	6.03
2	5.44	5.04	4.87	2.07	29.20	68.73	11.88	0.23	1.93	582.9	1.85	5.75
3	5.28	5.11	2.94	2.73	29.10	68.17	17.05	0.21	1.47	459.6	2.26	6.49
4	5.52	4.28	3.41	1.85	22.45	75.70	28.51	0.22	1.59	497.7	2.42	6.37
5	6.26	3.48	3.03	2.48	22.58	74.94	19.41	0.18	1.43	453.3	1.98	5.47
6	5.30	5.45	5.42	2.77	31.93	65.30	17.57	0.21	1.93	515.9	2.50	7.30
7	5.53	6.26	2.94	2.77	35.78	61.45	15.82	0.19	1.73	504.3	2.40	6.86
8	5.42	4.89	3.12	2.85	31.20	65.95	14.83	0.15	1.48	462.4	2.16	6.35
9	5.48	4.40	3.31	2.74	30.76	66.50	17.67	0.22	1.22	375.2	2.15	5.80
10	6.13	4.93	4.60	3.33	29.00	67.67	27.75	0.13	1.19	538.4	2.53	6.14
11	5.89	2.76	5.98	3.56	32.51	63.93	40.21	0.08	1.19	508.4	2.51	4.70
12	5.56	3.36	4.31	3.39	31.39	65.22	36.45	0.14	1.61	517.9	2.77	5.97
13	5.43	3.16	4.69	3.59	33.74	62.67	29.27	0.08	2.64	446.3	2.32	5.08
14	6.12	3.69	5.34	4.26	32.14	63.60	55.13	0.11	2.03	543.9	3.09	5.57
15	5.12	3.39	5.15	4.43	37.60	57.97	19.41	0.11	2.47	346.3	2.22	5.17
16	5.09	3.88	5.06	4.58	36.16	59.26	21.72	0.21	1.45	290.9	2.61	5.43
17	5.16	3.82	5.52	2.40	26.86	70.74	13.59	0.17	1.28	317.3	2.02	5.34
18	5.17	3.98	4.87	2.40	26.88	70.72	19.09	0.12	1.23	366.6	2.22	5.98
19	5.25	3.90	5.70	2.52	31.00	66.48	15.82	0.16	1.69	342.0	2.23	5.89
20	5.41	3.78	4.87	1.99	27.07	70.94	15.62	0.14	1.40	345.1	2.25	6.20
Ave	5.53	4.16	4.45	2.90	29.84	67.26	22.64	0.16	1.61	439.8	2.33	5.89
Std	0.37	0.88	1.01	0.87	4.68	5.40	10.81	0.05	0.41	86.9	0.29	0.62
CV%	6.63	21.13	22.60	29.80	15.67	8.02	47.75	29.08	25.57	19.8	12.56	10.53
Max	6.26	6.26	5.98	4.58	37.60	79.16	55.13	0.23	2.64	582.9	3.09	7.30
Min	5.09	2.76	2.94	1.37	19.47	57.97	11.88	0.08	1.19	290.9	1.85	4.70
Median	5.43	3.89	4.78	2.75	30.88	66.49	18.38	0.16	1.48	456.5	2.25	5.93
Soil uncontaminated by W mining (P3 site – control)												
1	6.28	4.94	5.52	5.06	41.47	53.47	9.29	0.19	0.68	179.6	1.95	5.11
2	5.91	5.24	5.14	1.63	20.39	77.98	5.34	0.26	0.72	175.1	1.91	5.43
3	6.07	4.66	5.33	2.09	23.70	74.22	6.69	0.12	0.82	98.1	1.55	5.03
4	5.52	5.65	5.51	3.55	32.91	63.54	5.29	0.21	0.94	103.6	1.72	6.34
5	5.66	5.43	4.87	3.65	32.97	63.38	10.86	0.19	0.82	163.2	2.33	6.24
6	6.16	5.74	5.25	5.26	39.38	55.36	11.54	0.45	0.82	241.7	2.58	6.36
7	5.89	3.79	5.61	1.87	24.20	73.93	8.15	0.14	0.54	105.1	1.85	4.30
8	5.26	3.73	3.95	5.08	36.03	58.89	4.62	0.12	0.67	122.8	1.97	5.09
9	5.63	4.83	5.98	4.78	38.31	56.91	6.48	0.12	0.72	86.0	1.66	5.09
10	5.35	5.37	5.52	3.55	29.86	66.59	7.16	0.11	0.94	119.5	1.95	6.05

Table 1. Continued.

Sample	pH	OM	Carb	Clay	Silt	Sand	As	Hg	Tl	Mn	Fe	Al
		%	g/kg	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	%	%
Ave	5.77	4.94	5.27	3.65	31.92	64.43	7.54	0.19	0.77	139.5	1.95	5.50
Std	0.34	0.71	0.55	1.40	7.24	8.60	2.38	0.10	0.12	49.0	0.31	0.70
CV%	5.95	14.39	10.43	38.30	22.67	13.35	31.51	54.05	16.28	35.1	15.72	12.79
Max	6.28	5.74	5.98	5.26	41.47	77.98	11.54	0.45	0.94	241.7	2.58	6.36
Min	5.26	3.73	3.95	1.63	20.39	53.47	4.62	0.11	0.54	86.0	1.55	4.30
Median	5.77	5.09	5.42	3.60	32.94	63.46	6.93	0.16	0.77	121.2	1.93	5.27
Jiangxi soil							14.90	0.08	0.88	328.0	2.88	8.60
China soil							11.20	0.07	0.62	583.0	2.94	6.62
World soil							6.00	0.06	0.20	600.0	4.00	7.10
Upper continental crust							2.00	0.06	0.75	527.0	3.09	7.74

mine in Dayu County. Therefore, the soils around W mines may be contaminated by various toxic trace elements from W mining.

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