

Assessing anthropogenic sources of mercury in soil in Wanshan Hg mining area, Guizhou, China

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Abstract Long-term mining and smelting activities brought a series of environmental issues into soils in Wanshan mercury (Hg) mining area (WMMA), Guizhou, China. Several studies have been published on the concentrations of Hg in local soils, but a comprehensive assessment of the mass of Hg in soil induced by anthropogenic activities, as presented in this paper, has not been previously conducted. Three districts of WMMA were chosen as the study areas. We summarized previous published data and sampled 14 typical soil profiles to analyze the spatial and vertical distributions of Hg in soil in the study areas. The regional geologic background, direct and indirect Hg deposition, and Hg-polluted irrigation water were considered as the main sources of Hg contaminations in local soils. Furthermore, the enrichment factor (EF) method was applied to assess the extent of anthropogenic input of Hg to soil. Titanium (Ti) was chosen to be the reference element to calculate the EF. Generally, the elevated values of EF were observed in the upper soil layers and close to mine wastes. The total budget of Hg in soil contributed from anthropogenic sources was estimated to be 1,227 t in arable soil and 75 t in natural soil.

Our data showed that arable soil was the major sink of anthropogenic Hg in the study area.

Keywords Mercury · Anthropogenic sources · Soil · Wanshan mercury mining area

Introduction

The emissions of mercury (Hg) contributed by natural and anthropogenic sources associate with its biogeochemical cycling in the environment. As soon as emitted into the atmosphere, Hg could be deposited to terrestrial and aquatic environments or be eventually converted to more toxic forms such as methylmercury (MeHg; Engstrom and Swain 1997; Munthe et al. 2007). Hg emissions from coal combustion and non-ferrous metal smelting contribute the majority of total anthropogenic Hg emissions, and it was estimated that these two sources accounted for almost 80 % of the total global Hg emissions to the atmosphere (Selin et al. 2007; Lindqvist 2007). It is estimated that Hg deposition fluxes increased three times and that the surface soil Hg reservoir increased by 10–15 % since industrialization due to enhanced Hg emissions from human activities (Selin et al. 2008; Yang et al. 2010). In China, the total annual anthropogenic Hg emissions to the atmosphere has been estimated to be in a range of 500–700 tons, which seriously threatens the qualities of the local environments, especially the terrestrial compartment (Fu et al. 2012).

The soil compartment is both a potential source and sink of Hg in the global Hg cycle (Kim and Lindberg 1995). More than 90 % of the continental deposition of Hg occurs in soils, and Hg could bind to organic matters once entering into the soils (Lindqvist 1991; Fitzgerald 1995). Inorganic Hg could be converted to MeHg under favorable conditions,

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which may cause adverse health effects to human beings via food consumption (Ullrich et al. 2001). In particular, Meng et al. (2010) indicated that newly deposited Hg appeared to be more labile toward transformation to MeHg in paddy fields and consequent accumulation in rice. In China, recent studies implied that the consumption of rice rather than fish was the primary pathway of human MeHg exposure to indigenous populations in inland Hg mining areas (Feng et al. 2008; Qiu et al. 2008; Zhang et al. 2010). Unlike the natural sources, Hg of anthropogenic origins is usually expected to be accumulated in the topsoil via atmospheric deposition. Hg accumulated in the soil compartment may be subjected to reemission to the air, which constitutes the secondary sources of Hg contamination in the air (USEPA 1997).

To distinguish heavy metals between natural origin and anthropogenic origin is of vital importance for environment protection and management. Numerous ways have been used to distinguish the origins of heavy metals in the environment, including statistical and geochemical methods as well as regulatory reference value method (Matschullat et al. 2000). A common approach to estimate the anthropogenic impact on soils is to calculate a normalized enrichment factor (EF) for metal concentrations above uncontaminated background levels. Due to its universal formula, the enrichment factor is a relatively simple and easy tool for assessing the enrichment degree and comparing the contamination of different environmental media (e.g., Atteia 1994; Blaser et al. 2000a, b; Veyseyre et al. 2001). With the increasing emission of traffic exhaust, agricultural activities, and industrial effluent, heavy metals, such as Hg, Cd, and Pb, are considered as the most serious pollutants due to their persistence and high toxicity in the environment. The EF method became a convenient and important tool to determine these contaminants in soils and distinguish the anthropogenic impact on the cycling of heavy metals (e.g., Ye et al. 2011; Zhang et al. 2008; Wang et al. 2010). The EF method normalizes the measured heavy metal content with respect to a sample reference metal such as Fe, Al, and Ti (Reimann and de Caritat 2000). Under different regional natural backgrounds, soil element contents can vary by several orders of magnitude (Anderson and Kravitz 2010). Moreover, there is no real pristine area on our planet anymore because of the ubiquitous long-range transboundary transport of pollutants in the atmosphere (e.g., Bindler et al. 1999). Therefore, the content of a reference element in deep soil layers was considered to be a reasonable approach to calculate the value of EF (Reimann and de Caritat 2005; Bourennane et al. 2010).

Wanshan Hg mine, located in the circum-Pacific mercuriferous belt (Gustin et al. 1999), was the largest conglomeration of Hg deposits in Guizhou, SW China (Feng and Qiu 2008). Undergoing approximately 3,000 years of Hg mining activities, large-scale Hg mining and retorting were shut down in 2001 in Wanshan, and about 22,000 t of Hg and 6,000 t of cinnabar ores had been produced (Qiu et al.

2005). Significant quantities of gangues and mine tailings (calcines) were stockpiled near the abandoned Hg processing sites. Between 1949s and 1990s, a total amount of about 20 billion cubic meters of Hg-containing exhaust gas had been dispersed into ambient air (Feng and Qiu 2008). Nowadays, Hg has been diffused into various compartments of the environment in Wanshan mercury mining area (WMMA). Several studies have previously documented high concentrations of Hg in soil in WMMA, ranging from 0.10 to 790 mgkg⁻¹ (Ding et al. 2004; Liu 2006). The concentrations of total mercury in ambient air were 17.8–1,101.8 ngm⁻³, with Hg emission flux of 162–27,827 ngm⁻²h⁻¹ from the soil to the air (Horvat et al. 2003; Qiu et al. 2008; Li et al. 2009; Zhang et al. 2010; Feng and Qiu 2008). However, the total reservoir of Hg stored in surface soil originated from Hg mining activities in WMMA is still unknown.

The objectives of our study were to (1) present the spatial distribution of Hg in the soil compartment and (2) to evaluate the Hg budget in soil that originated from anthropogenic sources in WMMA on the basis of statistical and geochemical methods.

Materials and methods

Area description

The study area (Wanshan catchment, WSC), being a part of WMMA, covers an area of 169.47 km² including Wanshan town, Aozhai ethnic town, and Xiaxi ethnic town, as shown in Fig. 1. The region belongs to a typical karst terrain with elevations ranging from 205 to 1,150 m a.s.l. It represents a subtropical humid climate with abundant precipitation (1,200–1,400 mm year⁻¹) and a mild temperature (~17 °C).

The major rivers in WSC include the Xiaxi and Aozhai Rivers with their headwaters originating from Hg mining sites. Large quantities of low-grade ores and calcines are stockpiled in their upstream banks and/or flood plains. A large swathe in the north of Aozhai River along the direction of Gouxu has a number of artisanal Hg retorting units.

The arable lands cover 24.02 km², of which 64.9 % is rice paddy fields. Both rivers are the irrigation water resources for farmland distributed in or near the banks of the rivers. Low shrubs and forests are the dominant land uses. Red earth–ultisol, ultisol, limestone soil, and paddy soil are the developed soil types in the study area.

Sampling procedures

Using a metal corer with a diameter of 40 mm and length of 2 m, intact soil profiles were manually collected from eight locations in the arable field (paddy soil and dryland) and six locations in natural soil (meadow soil and forest soil). Soil

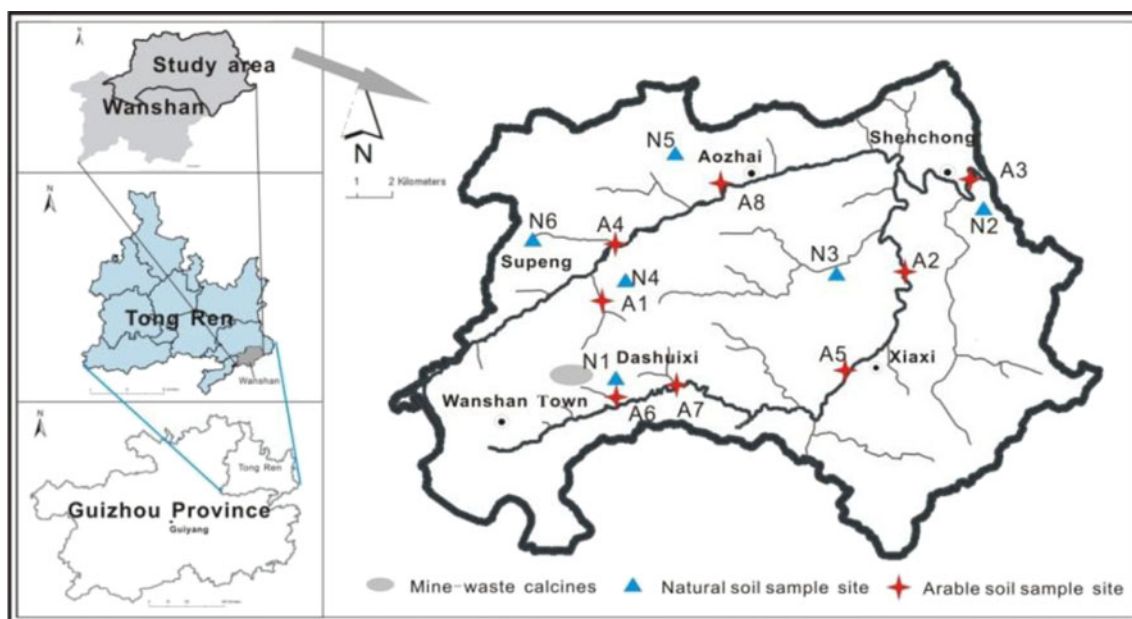


Fig. 1 Study area and the locations of the sampling sites

samples were collected with a depth of 10 cm on the surface soil and with 5-cm interval after 10 cm in depth. Soil samples in different horizons were contiguous in each soil column. The soil samples collected from the bottom of the soil profiles represent the pure parental materials.

Another metal core with 50-mm diameter and 50-mm length was used to determine the bulk density of soil in situ (Grossman and Reinsch 2002). During the sampling, a bamboo blade was used to strip the surface of contact with metal samplers. Three hundred fifty-four randomly selected sample sites were chosen to measure the thickness of soil layers in WSC. Thicknesses and corresponding GPS data were recorded at the same time during the sampling period.

All soil samples, except for those used for measuring the bulk density, were air-dried, ground in a ceramic disc mill, and sieved to a 200-mesh. Appropriate amounts (0.3–0.5 g dry weight) were taken for sample analysis (Qiu et al. 2006). While collecting, storing, and transporting the soil samples, we have followed the procedure recommended by USEPA method 1631 (USEPA 2002).

Laboratory examination of soil samples

Hg concentrations, organic matter (OM) contents, and reference element contents were analyzed in this study. To determine the Hg concentrations, soil samples were digested in a water bath (95 °C) using a fresh mixture of concentrated HCl and HNO₃ (3:1, v/v). Then, a suitable aliquot of the digested sample solution was measured by cold vapor atomic absorption spectrometry using a F732-S spectrophotometer (Shanghai Huaguang Machinery and Instrument Company, China; Li et al. 2005). Quality assurance and quality control

of Hg analysis were determined using duplicates, method blanks, matrix spikes, and certified reference materials (GBW070009, GSB10020). The recovery for standard reference materials was in the range of 84–102 % and the relative percentage difference of sample duplicates was <8 %. OM contents in soil samples were measured by a titration method using FeSO₄ after the digestion of samples with a K₂Cr₂O₇–H₂SO₄ solution (Schulte 1995). The contents of reference elements, titanium (Ti), in soil which are immobile and originate almost exclusively from the bedrock were measured based on the X-ray fluorescence (model XLt, Thermo Scientific Niton) method (USEPA 1998). The instrument was kept steadily on top of the soil surface, with an X-ray exposure and X-ray fluorescence signal collection time of approximately 100 s. In determining the soil bulk density, soil cores collected by the bulk soil corer were pushed out of the sampler and individual soil samples were weighed and then dried at 105–110 °C. Finally, it was reweighed to determine gravimetric soil moisture on a dry weight basis (Ellert and Bettany 1995).

EF calculation

The EF method was initially developed to speculate on the origins of elements in the atmosphere, precipitation, or seawater (e.g., Buat-Menerd and Chesselt 1979). Subsequently, it was progressively extended to quantify the extent of human-induced contamination in soil, sediments, and other environmental materials, generalized as shown in Eq. 1 (Reimann and de Caritat 2000).

$$EF = \frac{C_{\text{sample}}/X_{\text{sample}}}{C_{\text{crust}}/X_{\text{crust}}} \quad (1)$$

where C is the concentration of the element under consideration (in milligrams per kilogram) and X is the concentration of the chosen reference element. The subscripts “sample” and “crust” indicate which medium the concentration refers to.

As the commonly used reference element in the literature, Ti was measured to calculate the values of EF (Blaser et al. 2000a, b; Reimann and de Caritat 2000). In our study, Ti was used as the reference element for geochemical normalization because of the following reasons: (1) it usually occurs in much higher concentrations than the other reference elements, (2) its geochemistry is similar to that of many trace metals, and (3) its natural concentration tends to be uniform (Liu et al. 2004). Generally, if the EF of an element is <1 , it may indicate that this element is entirely originated from bedrock weathering (e.g., weathering product). When the EF of an element is larger than 1, it is considered that this element is enriched in soil and that the enrichment of this elements is derived from anthropogenic activities. The interpretation of EF is shown in Table 1.

Estimating the budget of Hg contributed from anthropogenic activities in soil

The budget of Hg induced by human activities in the soil compartment in WSC was calculated using the following equation:

$$M = 225.2$$

$$\sum_z \left[\sum_{i,j} \left(EF_{ij} \cdot \frac{X_{sample,ij}}{X_{crust,ij}} - 1 \right) \cdot C_{crust,ij} \cdot B_{ij} \cdot h_{ij} \right] \tag{2}$$

where M is the mass of Hg in soil (in grams), B is soil bulk density (in grams per cubic meter), h is the thickness of the calculated unit (in centimeters), and i, j , and z are space coordinates, described in Fig. 2. The area of each computing unit is 225.2 cm^2 .

In this study, soil bulk density (B) and water content in soil (d) were taken to calculate the mass of Hg in soil. They are described by the following two equations:

$$d = (W_1 - W_2)/W_2 \times 100 \tag{3}$$

$$B = 100 \times W_1/[V \times (100 + d)] \tag{4}$$

where d is the soil moisture content (in percent), W_1 is the mass of wet soil (in grams), and W_2 is the mass of dry soil (in grams).

To determine the values of i and j in every calculated column, ordinary kriging interpolation method was applied to simulate the thickness of soil in the whole area. We utilized 354 data of thicknesses of the soil layers as the control points to interpolate a map of soil thickness in WSC.

The following assumptions were applied to ensure the calculation to be more reasonable. First of all, we assumed the soil in one computing unit to have uniform physico-chemical properties. Secondly, we neglected the anomalies of soil thickness in the study area. Besides, the Thiessen polygon method was used to divide the study area into subunits, and the centers of the subunits were placed at the sites where the soil profiles were collected (Gibson et al. 2006). The area of the calculated unit is 15×15 pixels, divided by the software of ArcGIS 9.3.

Results

Distributions of Hg in soil

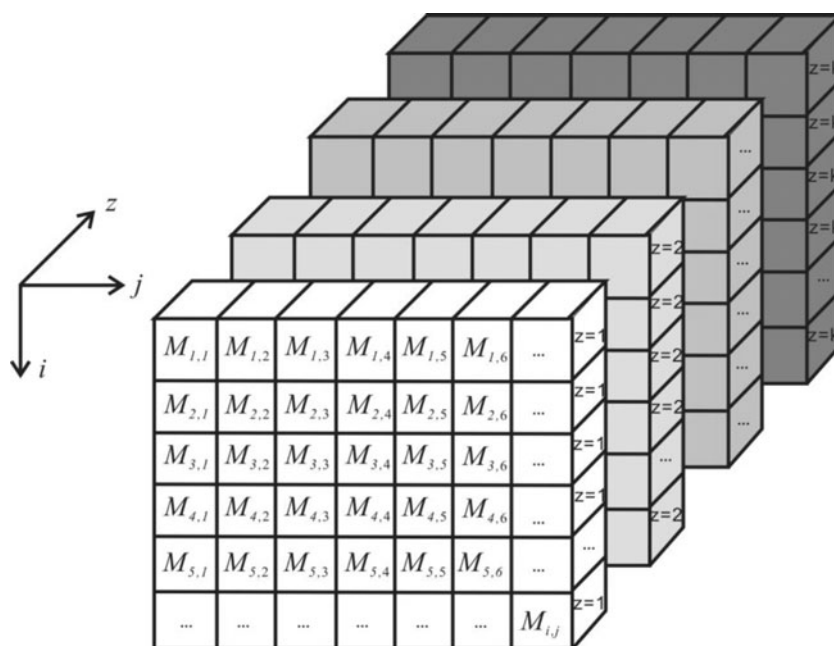
A comprehensive analysis of data on Hg concentrations in the surface soil in WSC collected from the previous publications showed a large variation of Hg concentrations in soil, not only from different soil categories but also from soil with different distances from the mine calcines, ranging from 0.10 to 790 mg kg^{-1} , as described in Table 2 (Horvat et al. 2003; Ding et al. 2004; Qiu et al. 2005; Xu 2008; Lin et al. 2009). All data overwhelmingly pinpointed that highly elevated concentrations of Hg have been observed around the piles of Hg mine wastes and calcines and decreased rapidly after a distance of 4–8 km from the mine wastes and calcines.

Figure 3 indicates that the distributions of Hg varied in the soil profiles sampled in different land uses. In natural soil, Hg concentrations gradually decreased with depth along the soil profiles, and Hg concentrations in all soil samples correlated significantly with organic matter contents (e.g., $r=0.868$, $p<0.01$ in the profile of N1; $r=0.579$, $p<0.05$ in the profile of N4). In general, Hg concentrations decreased rapidly with depth below 20 cm in soil profiles, whereas in arable soil, no obviously changing trend and no correlation between Hg and OM were observed in most soil profiles. Hg concentrations and OM contents in soil showed positive correlations in the profiles of A1 and A4, with

Table 1 Classification of enrichment factors (Sutherland 2000)

EF value	EF class	Designation of element quality
<1	0	Uncontaminated
1–2	1	Depletion to minimally contaminated
2–5	2	Moderately contaminated
5–20	3	Significantly contaminated
20–40	4	Strongly contaminated
>40	5	Extremely contaminated

Fig. 2 Description of the x , y , and z space coordinates



correlation coefficients of 0.952 ($p < 0.01$) and 0.922 ($p < 0.01$), respectively. Hg concentrations in soil ranged 12.5–572 and 6.6–53.83 mg kg^{-1} at A1 and A4, respectively.

The budget of Hg in soil from anthropogenic contribution

The classifications of EF in different soil profiles are shown in Fig. 4. The values of EF, using Ti as the reference element, were in the range of 0.1–33.07. According to the threshold of EF, the layers with no anthropogenic disturbance were determined. The high EF values were observed in arable soil around calcine wastes (<4 km). In contrast, the extents of anthropogenic disturbance were lower in the soil far away from calcine wastes and especially for the natural soil. In addition, the EF values also exhibited obviously vertical distributions, which were higher in the upper layers than those in lower horizons. In accordance with Eq. 2, the budgets of Hg in soil induced by anthropogenic activities are calculated to be 1,227 t in arable soil and 75 t in natural soil in WCS, which were listed in Table 3.

Discussion

Sources of Hg in soil

Hg concentrations in soil in WMMA were higher than those in worldwide uncontaminated soils (0.01–0.050 mg kg^{-1} ; Senesil et al. 1999). Significant differences in both the amount and distribution of Hg in soils suggested different origins of mercury from site to site. First of all, the elevated Hg geochemical background in bedrock can contribute to the elevation of Hg in soil, and the geochemical background of Hg in bedrocks may span a wide range (Qiu et al. 2005). Additionally, previous studies demonstrated that Hg emission from historical large-scale Hg retorting, current artisanal Hg retorting operations, and calcine heaps could impact significantly the soil compartment via the wet/dry deposition of Hg from ambient air as dry/wet Hg deposition was usually considered as the main Hg contamination source to soil (Qiu et al. 2005). Besides, a number of studies (i.e., Ericksen et al. 2003; Meng et al. 2012) revealed that almost all of Hg in foliar tissues is originated from the atmosphere,

Table 2 Concentrations of Hg in topsoil in different land uses (in milligrams per kilogram)

Hg mining wastes	Paddy soil	Dryland	Meadow soil	Forest soil	References
	0.10–790	0.30–740			Qiu et al. (2005)
245.4–347.5	24.3–123				Ding et al. (2004)
	8.0–130				Lin et al. (2009)
34.1–18.9	8.1–156	16.3			Horvat et al. (2003)
197.5–239.2					Xu (2008)
	0.2–389		0.1–312	0.1–299	Dai et al. (in preparation)

and Hg in roots came mainly from soil. Therefore, litterfall is another pathway of the atmospheric deposition of Hg to soil. Moreover, the elevated Hg concentrations in arable soil, especially the paddy soil, were apparently also originated from irrigation with Hg-polluted surface water (Qiu et al. 2005; Zhang et al. 2010).

The distributions of Hg and OM were discrepant in different land uses. In all soil profiles sampled in natural soil, significantly positive correlations between Hg concentrations and OM content in soil were observed, and the source of Hg contamination was mainly derived from direct wet/dry deposition from ambient air. Organic matters can strongly absorb Hg and act as filters for Hg in surface soil (Lindqvist 1991). That may be the cause of Hg concentrations decreasing rapidly with depth below 20 cm in soil profiles. A comparison of the relations of Hg and OM in

different soil profiles sampled in arable soil revealed that there was no correlation between Hg concentration and OM content in most soil profiles. Zhang et al. (2010) discovered that the concentrations of total Hg (THg) were highly dominated by and correlated with particulate mercury (PHg) in surface water in WMMA, and PHg could account for 99.6 % of the THg in surface water close to the mine wastes. In WSC, seasonal irrigation brought a great quantity of Hg-polluted runoff into paddy fields, and all Hg in irrigation water were bound with particulate matter. Therefore, no significantly positive correlation between Hg concentration and OM content in soil was observed in arable soil in WSC. It is noted that there were fluctuations of Hg concentrations within horizons of 0–30 cm in all arable soil profiles. Conventional tillage usually resulted in the redistribution of Hg in soil profiles, which may be another factor to result

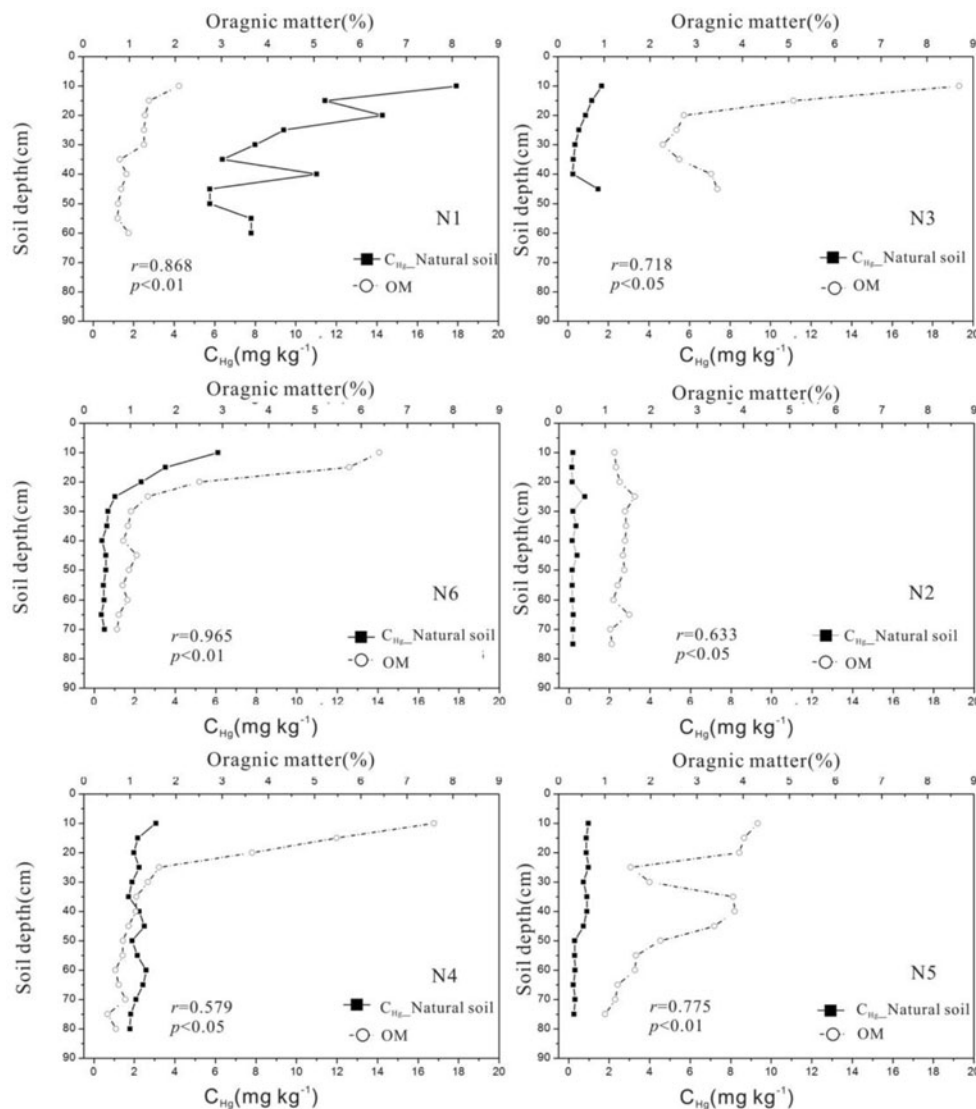


Fig. 3 Distributions of Hg and OM in different soil profiles (N1–N5 are soil profiles sampled in natural soil; A1–A8 are the profiles sampled in arable soil)

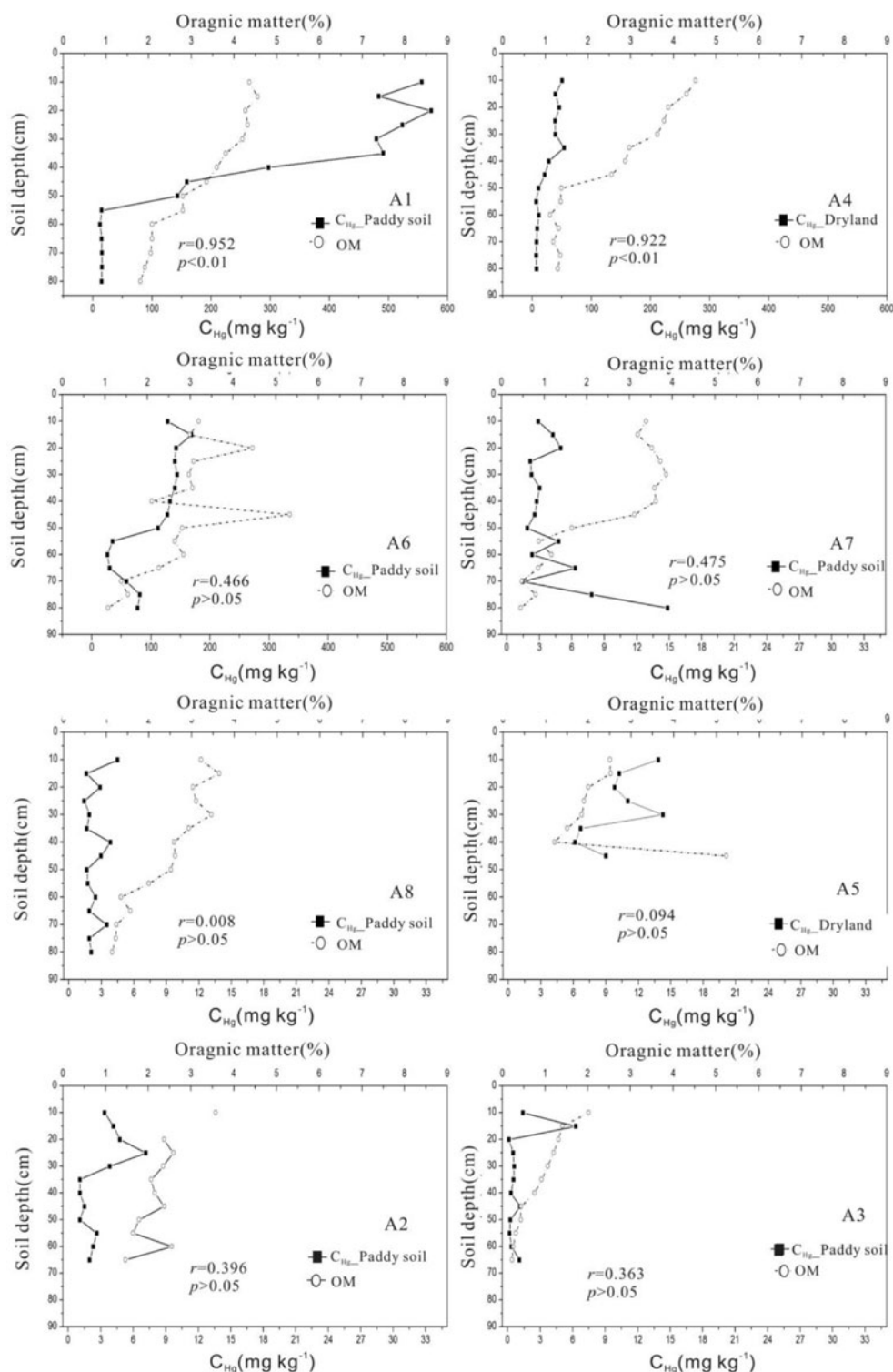
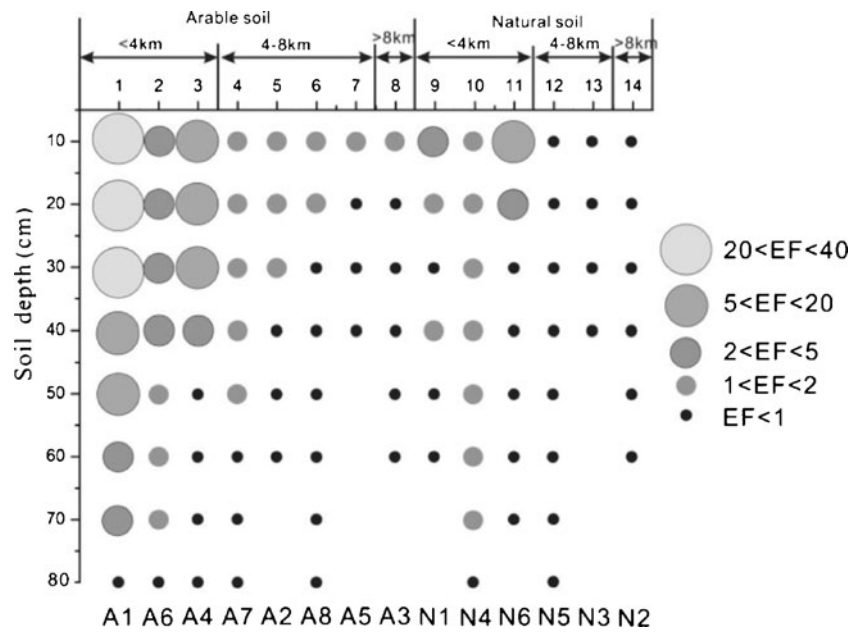


Fig. 3 (continued)

in the non-correlation between Hg concentration and OM content in paddy fields and dryland (e.g., the profile of A5). Particularly, significantly positive correlations between Hg concentration and OM content in soil were observed in soil profiles A1 and A4. Taking the geographical positions into

account, A1 and A4 sample sites were located along the downstream of Aozhai River and adjacent to the area of artisanal Hg retorting operations. Hg concentrations in soil at A1 site were usually the highest among all soil samples, as reported by Qiu et al. (2005) in WMMA. A previous

Fig. 4 Classifications of EFs in different soil horizons in Wanshan catchment



study showed that the corresponding concentrations of Hg in surface water at site A1 were not high during both high flow, normal flow, and low flow periods (Zhang et al. 2010). As a result, the significantly elevated Hg concentrations in soils at site A1 were not originated from surface water irrigation. The most possible source of Hg contamination at site A1 was the direct atmospheric deposition of Hg which was emitted into ambient atmosphere from the ongoing artisanal Hg retorting activities using indigenous techniques. The wet/dry deposition of Hg from the atmosphere

was also regarded as the main source of Hg contamination in soil at site A4 due to the fact that rainfall was the major irrigation water source of the dryland in the study area.

Assessment of anthropogenic contributions

The analysis of EF values implied that there was a wide stretch of soil with no or less Hg pollution downstream of the study area. Human-induced contamination of Hg usually occurred in the upper soil horizon, especially close to the

Table 3 Total budget of Hg in arable and natural soils contributed from anthropogenic sources (in tons)

Depth (cm)	Budget of Hg in arable soil (t)								Budget of Hg in natural soil (t)		
	A1	A6	A4	A7	A2	A8	A5	A3	N1	N4	N6
10	191.38	41.97	12.19	1.27	0.26	5.36	8.20	7.41	13.18	2.02	1.07
15	240.90	41.69	3.89	1.18	4.05	1.19			9.37	1.78	6.01
20	160.53	49.05	6.85	1.18	4.17	2.59			10.49	1.25	4.80
25	76.34	31.14	3.73	1.28	2.38	1.00			9.04	1.96	1.61
30	35.62	38.26	3.78	1.16	2.60				0.30	1.73	
35	4.48	31.98	17.84	1.12					0.25	1.94	
40	5.10	28.58	2.34	1.28					3.11	1.11	
45	5.49	26.48	50.63	1.32					2.55	0.67	
50	4.92	21.08		1.16						0.31	
55	0.87	9.27								0.20	
60	4.65	7.33								0.11	
65	0.77	8.97								0.09	
70	0.85	8.77								0.10	
Subtotal (t)				1,227						75	

pollution sources. Our calculation results revealed that Hg in arable soil contributed up to 94.7 % of the total Hg mass in WSC. It is well known that MeHg is a persistent bioaccumulative toxic pollutant which could be transformed by inorganic mercury. Under favorable conditions such as anaerobic conditions, inorganic Hg could be converted to MeHg (Ullricha et al. 2001; Qiu et al. 2005). In the paddy fields, anaerobic conditions produced by seasonal irrigation in surficial soil and the abundant supplement of Hg from Hg-polluted irrigation water favored the in situ methylation of inorganic Hg (Gilmour and Henry 1991; Qiu et al. 2005). Our data showed that arable soil was the major sink of anthropogenic Hg in WSC; rice paddy in WCS could be a hot spot for MeHg production and accumulation in the food chain, which poses health risk to local inhabitants.

Conclusions

The spatial and vertical distributions of Hg in soil in WSC were characterized by analyzing previously published data on Hg distribution in soil and soil Hg distribution in the soil profiles collected in this study. Positive correlations between Hg concentration and OM content in all soil profiles sampled in natural soil were observed, while no significant correlations were observed in almost all soil profiles collected from arable soil. Geochemical background in bedrocks, emission from historical large-scale Hg retorting, current artisanal Hg retorting operations and calcine heaps, litterfall, and Hg-polluted irrigation water were considered to be important sources of Hg in soil in WSC. At the same time, the values of EF were applied to assess the extent of anthropogenic input of Hg to soil. Ti was considered to be the fittest reference element to calculate the value of EF compared to other different reference elements. Generally, elevated values of EF were observed in the upper soil layers and the soil close to mine wastes. Calculations utilizing EF showed that the masses of Hg in soil induced by anthropogenic sources are 1,227 t in arable soil and 75 t in natural soil in WSC. Our data showed that arable soil was the major sink of anthropogenic Hg in WMMA.

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