Total mercury and methylmercury in the soil and vegetation of a riparian zone along a mercury-impacted reservoir

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HIGHLIGHTS

- THg, MeHg concentrations were measured in riparian plants from Hg-impacted reservoir.
- THg concentrations decrease along riparian zones due to the pollution from GOCP.
- Hg level in riparian plants is affected by physiological features, soil Hg level.
- TFs for THg >1 have the potential for phytoextraction in Hg-impacted riparian zones.

GRAPHICAL ABSTRACT
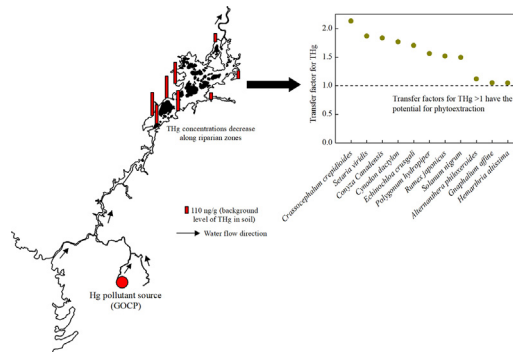
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ABSTRACT

The Baihua Reservoir (Guizhou Province, Southwest China) has a history of mercury contamination associated with past acetic acid production activities at the Guizhou Organic Chemical Plant (GOCP). Soil and plant samples collected from riparian zones were analyzed for total Hg (THg) and methylmercury (MeHg) using cold vapor atomic fluorescence spectroscopy. The concentrations of THg and MeHg in soil samples were in the range of 109–371 ng g^{-1} and 0.32–1.80 ng g^{-1}, respectively. Soils in the riparian zones close to the pollution source (the GOCP) presented higher Hg contamination, with relatively light Hg contamination in remote areas. This suggests a decreasing trend of THg concentrations along the riparian zones, with higher concentrations closer to the pollution source. Significant correlations were found between MeHg and soil organic matter ($n = 24$, $p = 0.01$). THg concentrations varied 11.3–161 ng g^{-1} in aboveground areas and 11.3–193 ng g^{-1} in underground areas. MeHg concentrations ranged from 0.23 to 1.06 ng g^{-1} in aboveground areas to 0.13–1.51 ng g^{-1} in the below ground areas. The vegetation studied showed different concentrations of THg and MeHg and can be considered to be impacted by Hg contamination. Different concentrations of total and methyl mercury were found among the different plant species. The high Hg concentrations in soils and vegetation suggests that the ability of Hg to bioaccumulate in riparian plants is affected by plant physiological characteristics and soil mercury concentrations. Although the bioaccumulation factors (BCFs) of the studied plants were low, their transfer factors (TFs) were >1. Our findings suggest that vegetation exhibiting TFs for THg >1 have the potential for phytoextraction in Hg-impacted riparian zones.

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1. Introduction

Mercury (Hg) is an element in the earth's crust and has no physiological benefits to the human body. Methylmercury (MeHg) is among the most toxic chemical forms of Hg in the environment and can be bioaccumulated in organisms (Mergler et al., 2007; Taylor et al., 2012). Biomagnifications of MeHg have been observed in freshwater and marine food chains (Campbell et al., 2005; Kidd et al., 2012; Kim et al., 2012). In recent decades, mercury contamination caused by human activities, such as coal combustion (Feng et al., 2002; Li et al., 2017; Perez et al., 2019), mining (Covelli et al., 2001; Qiu et al., 2006), and industrial production (Yan et al., 2008; Perez et al., 2019) is a global issue (Mergler et al., 2007), threatening the safety of local ecosystems and lives (Driscoll et al., 2007; Liang et al., 2017). Mercury contamination in various environments including reservoirs, is therefore associated with health risks.

Reservoirs are considered to be Hg-sensitive ecosystems (St Louis et al., 2004), due to damming and impounding and significantly altering the initial environmental conditions. The changes in environmental conditions have a profound impact on the Hg cycle in reservoirs (Hall et al., 2005; Zhao et al., 2017). For example, water impoundment results in the conversion of the initial soil environment from aerobic to anaerobic and promotes the decomposition of plant residues, ultimately stimulating the methylation of Hg (St Louis et al., 2004; Zhao et al., 2017).

Mercury concentrations in sediments (Yan et al., 2008), surface water (Feng et al., 2004), and aquatic organisms (Campbell et al., 2005; Kidd et al., 2012; Kim et al., 2012) increase due to the exogenous mercury contamination of reservoirs. In addition, this contamination extends beyond the reservoir and can also dramatically alter mercury processes in riparian ecosystems.

Contaminants can enter riparian zones from adjacent water (Lee et al., 2000; Vidon et al., 2010); as a result, riparian soils exhibiting high THg concentrations have been frequently reported in the literature (Jackson et al., 2019; Pant et al., 2011; Qiu et al., 2005b). A recent study has reported the methylation of Hg, attributed to the presence of methylating microorganisms, in riparian zones (Du et al., 2017). This methylation process is influenced by environmental factors such as Hg concentration and availability and organic matter (Liang, 2013; Meng et al., 2016). Furthermore, high concentrations of MeHg were found in riparian soils (Pant et al., 2011; Qiu et al., 2005b). Elevated Hg concentrations in riparian zones bring environmental risks and need to be investigated.

Many studies have demonstrated that Hg, including the highly toxic MeHg species (Witt et al., 2009), can be taken up by plant roots from soils. After root assimilation, mercury can be transported to the aboveground portion of the plant via the transpiration stream, and gradually exhibit a certain concentration (Qian et al., 2019). Therefore, plants may play a significant role in Hg transfer and accumulation in the
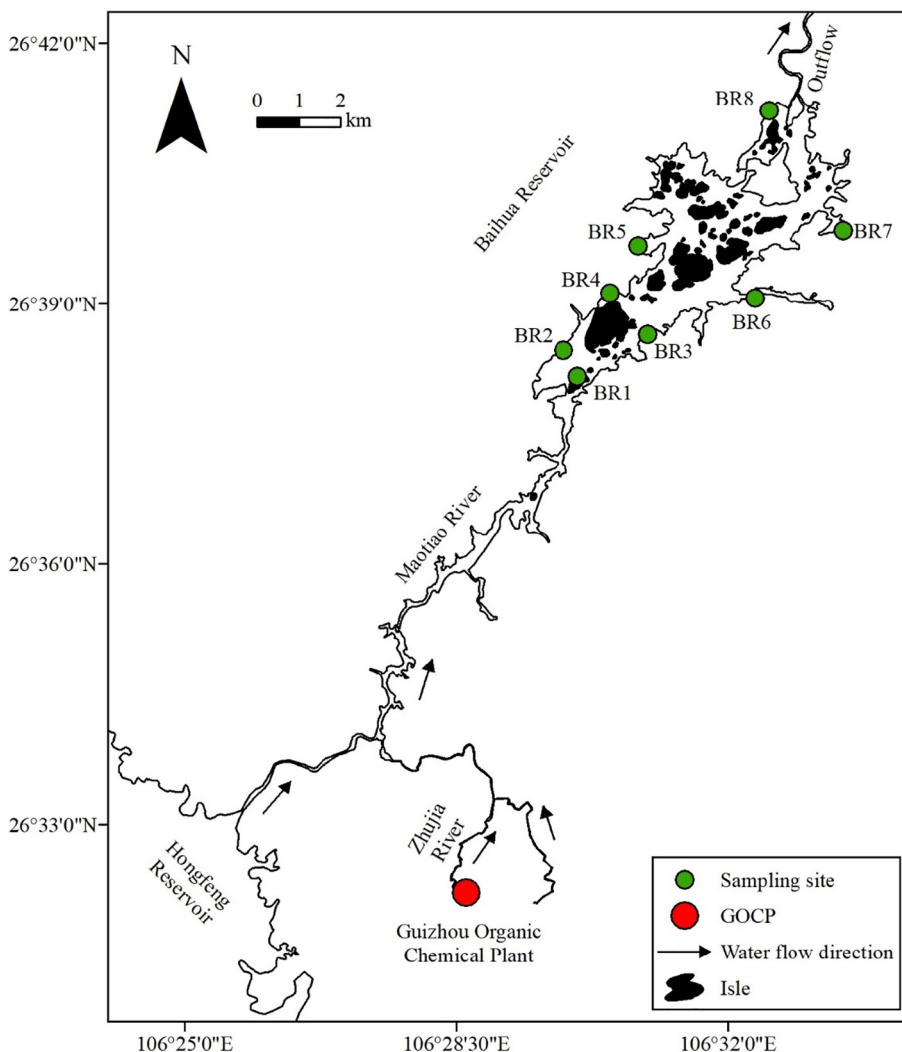

Fig. 1. The locations of the sampling sites.

environment. Studies have reported the potential of some plants for soil Hg phytoremediation (Fernandez-Martinez et al., 2015; Zhao et al., 2019). Increased concentrations of THg and MeHg in the riparian soils from contaminated reservoirs suggests an exposure risk to plants. Under this scenario, riparian plants may accumulate more Hg via roots. However, the distribution from the reservoir of Hg in the different morphological portions of riparian plants such as above and below ground, remains unclear. The bioaccumulation and transfer factor can be employed to analyze Hg transfer in soil-plant systems (Fernandez-Martinez et al., 2015; Qian et al., 2019).

The Baihua Reservoir (BR) was chosen for this study. It is the only known reservoir in China and is reported to have been heavily contaminated with Hg from the Guizhou organic chemical plant (GOCP), which used mercuric sulfate as a catalyst to produce acetic acid (Feng et al., 2010). The main objectives of this study are i) to evaluate the pollution risks of THg and MeHg in soils, and ii) to illustrate the distribution characteristics of THg and MeHg in riparian plants.

2. Materials and methods

2.1. Site description

The Baihua Reservoir (BR) (106°27′–106°34′ E, 26°35′–26°42′ N) was constructed and impounded in 1966. It is situated 16 km northwest of Guiyang City, the capital of Guizhou Province in southwest China. The BR is long and narrow (18 km long and 0.8 km mean width), with one main input flow and one output flow. Its watershed covers 1895 km^2. The climate of this area is subtropical, with rainy monsoons, an average annual rainfall of 1200 mm, and an annual mean temperature of 13.8 °C.

Between 1971 and 1997, the BR experienced severe Hg contamination (Feng et al., 2010; Yan et al., 2008) from the Guizhou Organic Chemical Plant (GOCP), which used mercuric sulfate as a catalyst to produce acetic acid. GOCP is located in the upper reach of the reservoir (Fig. 1). From 1971 to 1985, Hg-laden untreated effluents from GOCP were discharged directly into the Zhujia River and flowed into the BR. In 1985, the GOCP adopted a Hg removal device to prevent Hg discharge into the Zhujaia River and since 1997, GOCP has ceased using Hg technology to produce acetic acid. Table S1 shows the Hg levels in BR for different periods. For this work, soil and plant samples from the riparian zones were collected and examined.

2.2. Sample collection and preparation

Sampling was conducted in October 2016. For soil sampling, three parallel sub-sites were selected randomly at each sampling site. At each sub-site, five undisturbed samples were collected vertically from a soil depth of 0–20 cm and were mixed into a composite sample. Plant sampling followed a protocol described previously (Li et al., 2017). At each sampling site, plants growing well were selected randomly and retrieved in their entirety with a shovel. For transport to the laboratory, the composite soil and fresh plant samples were stored in clean polyethylene bags and stored in opaque plastic boxes with ice packs.

In the laboratory, coarse particles and biological debris were removed from the soil samples. The fresh plant samples were rinsed with tap water and then washed three times with ultrapure water (UW) to thoroughly clean the dirt. Each individual plant was divided into below ground and above ground biomass. The soil and plant samples were then freeze-dried in a dark environment.

The soil samples were ground through a 150 μm sieve. Plant samples were broken using a powder machine. The soil and plant powder samples were stored in clean polyethylene bags in a dark, cool environment (−20 °C) for further analysis. The THg and MeHg results are presented as dry materials in this study.

2.3. Sample analysis

2.3.1. THg analysis

The determination of THg in soil was performed by aqua regia digestion in a water bath coupled with cold vapor atomic fluorescence spectrometry (CVAFS) (Li et al., 2005). Approximately 0.2 g of dry soil sample was weighed into a pre-cleaned 25 mL glass colorimetric tube and 5 mL of UW and 5 mL of aqua regia (HCl:HNO$_3$ = 3:1, v/v) were added in turn and digested at 95 °C for 5 min in a water bath. Then, 1 mL of BrCl solution (2.7 g of guaranteed reagent KBr and 3.8 g guaranteed reagent KBrO$_3$ were dissolved in 250 mL of HCl) was added to digest continuously at 95 °C for 30 min. After cooling, the digestion solution was fixed to 25 mL with UW and then reacted for >24 h. Then, 0.2. mL of NH$_2$OH·HCl solution (25 g of guaranteed reagent NH$_2$OH·HCl was dissolved in 100 mL of UW) was added to the digestion solution to reduce excess BrCl solution. The pre-concentration of the clarified digestion solution was performed according to steps described in the literature (Liang et al., 2001). Finally, the determination of THg was performed by CVAFS (Model III, Brooks Rand, USA).

The digestion with HNO$_3$ was employed to analyze the THg in the plants (Zheng et al., 2006). Approximately 0.2 g of dry plant sample was weighed into a 25 mL glass colorimetric tube, 5 mL of HNO$_3$ was added, and the mixture was digested at 95 °C for 3 h in a water bath. Then, 0.5 mL of BrCl solution was added and allowed to react for >24 h, after which 0.2. mL of NH$_2$OH·HCl solution was added to the digestion solution to reduce excess BrCl solution. The next pre-concentration and analysis steps were consistent with the determination of soil THg, as described above.

2.3.2. MeHg analysis

The analysis of MeHg in soil was performed following He et al., 2004. Approximately 0.2 g of soil was placed into a clean 50 mL centrifuge tube and 1.5 mL of 2 mol L^{-1} CuSO$_4$ solution and 7.5 mL of 25% (v/v) HNO$_3$ were added, in turn. The extract and reverse extraction steps were performed. Then, 10 mL CH$_2$Cl$_2$ was added to the tube and shaken for 30 min. The tube was then centrifuged at 3000 rpm for 30 min. The CH$_2$Cl$_2$ layer was pipetted into another clean 50 mL centrifuge tube. Approximately 45 mL of UW was added to the tube which was placed in a water bath at 45 °C until the visible CH$_2$Cl$_2$ was volatilized. The temperature was then increased to 80 °C to remove the residual CH$_2$Cl$_2$ by pure nitrogen gas. The liquid in the tube was brought to 50 mL with UW. An appropriate volume (generally 15 mL) of the liquid was transferred to a pre-cleaned borosilicate glass bottle and brought to 80 mL with UW. The pH of the liquid was adjusted to 4.5. Finally, 0.1 mL of ethylation reaction reagent was added to the liquid, and the aqueous phase ethylation was reacted for 15 min under sealed conditions. After the tenax-collection step (Liang et al., 1994), MeHg was determined using CVAFS.

The digestion procedures for plant MeHg followed a previous method (Qiu et al., 2005a). Approximately 0.2 g of plant sample was weighed into a 50 mL centrifuge tube, then 5 mL of KOH solution (25 g of guaranteed KOH dissolved in 100 mL of UW) was added to the tube and digested at 75 °C for 3 h in a water bath. After cooling, the digestion solution was adjusted to acidity (pH = 1–2) with an appropriate HCl (approximately 3 mL) and then, the next extraction and reverse extraction steps were performed following the analysis procedure of soil MeHg as outlined above. Finally, MeHg determination was performed by CVAFS.

2.3.3. Determination of SOM in soil samples

The soil organic matter (SOM) concentration was measured by wet digestion (Meng et al., 2016). Approximately 0.1 g of dry soil sample was weighed into a cleaned centrifuge tube, with 10 mL of H$_2$SO$_4$ and 5 mL of 1 mol L^{-1} K$_2$Cr$_2$O$_7$ in a 100 °C water bath for 15 min. The digestion solution was transferred to a triangle bottle and fixed to 120 mL with UW. The solution was then titrated to red with 0.2 mol L^{-1} FeSO$_4$ solution under the indicator of o-phenanthroline.

2.3.4. Bioaccumulation factors and transfer factors

The bioaccumulation factor (BCF) and transfer factor (TF) from below to above ground were calculated using the following formula (Fernandez-Martinez et al., 2015):

$$BCF = C_{above}/C_{soil}$$

$$TF = C_{above}/C_{below}$$

where C_{above} is the concentration of THg in the above ground portion ($ng\ g^{-1}$), C_{below} is the concentration of THg in the below ground portion ($ng\ g^{-1}$), and C_{soil} is the concentration of THg in soil ($ng\ g^{-1}$).

2.4. QA/QC

Certified reference materials, method blanks, and sample replicates were employed as part of the analytical quality control of the THg and MeHg determination. The recovery of THg from the soil in GSS-5 (GBW07405) was between 101.2% and 120.5%, and for soil MeHg in ERM-CC580 the recovery was between 82.6% and 105.9%. Moreover, THg recovery in plants ranged between 96.3% and 107.3% in GSB-11 (GBW10020) and between 94.5% and 100.6% for MeHg in ERMI-464CE. The relative standard deviation (RSD) ranges for duplicate sample analysis of THg and MeHg were 1.0–13.1% and 0.6–5.7%, respectively. The method detection limits for THg and MeHg analysis were 6 $ng\ g^{-1}$ and 0.003 $ng\ g^{-1}$, respectively.

2.5. Statistical analysis

Statistical variations for Hg concentrations were determined using the ANOVA analysis at $p < 0.05$. Pearson Correlation Coefficient was conducted between different parameters. The significance level was set at $p < 0.05$.

3. Results

3.1. Hg in soils

Table 1 shows the concentration variations of THg and MeHg in riparian soils.

High THg concentrations were recorded at sites BR1, BR2, BR3, BR4, and BR5, and ranged between 304 and 371 $ng\ g^{-1}$. These results were approximately three times that of other sites (BR6, BR7, and BR8), indicating a significant variation (ANOVA, $p < 0.05$) of THg along the riparian zones.

No significant variation was found for MeHg concentrations in soil samples. However, it was significantly correlated with soil organic matter ($n = 24$, $p = 0.01$) (Fig. 2).

3.2. Hg in vegetation

For THg, the concentrations varied from 11.3 to 161 $ng\ g^{-1}$ (above ground) and 11.3–193 $ng\ g^{-1}$ (below ground). For MeHg, the concentrations ranged from 0.23 to 1.06 $ng\ g^{-1}$ (above ground) and 0.13–1.51 $ng\ g^{-1}$ (below ground). The vegetation examined showed different concentrations of THg and MeHg (Table 1).

The highest concentrations (193 $ng\ g^{-1}$) of THg were found in *Polygonum hydropiper* in its below ground plant portion. This species grows at the BR5 site, which has high THg concentrations in the soil. The concentrations of THg in below ground plant portions were higher than 100 $ng\ g^{-1}$ in *Solanum nigrum* (collected from BR5 site) and *Rumex japonicus* (BR3). The soils these plant species grow in had similarly high THg concentrations.

Higher MeHg concentrations in below ground plant portions were found in *Solanum nigrum* (BR3), *Conyza canadensis* (BR3), *Cynodon dactylon* (BR2), and *Gnaphalium affine* (BR2). These results were higher than 1 $ng\ g^{-1}$. Moreover, the soils collected from the BR2 and BR3 sites showed high MeHg levels.

Total Hg concentrations in plants were lower than those in soils. However, several plant species, for example, *Solanum nigrum* (BR3) and *Cynodon dactylon* (BR2), had higher MeHg concentrations in their biomass than that present in the soil.

3.3. BCF and TF

Vegetation can absorb mercury from the atmosphere (Qian et al., 2019; Zhao et al., 2019) and therefore, a correction of the BCF and TF by subtracting this proportion of Hg concentration was considered more feasible for evaluating the bioaccumulation and the transfer of Hg in the vegetation accurately. Fernandez-Martinez et al., 2015 reported that free elemental Hg absorbed from the atmosphere generally accounts for 7% of THg in vegetation grown in Hg-polluted soils. Based on this finding, the results of BCF and TF are shown in Fig. 3.

The range of BCFs for THg was 0.10–0.30. The highest value was found in *Echinochloa crusgali*. The TF values for THg were always higher than 1. *Crassocephalum crepidioides* showed the highest TF value.

4. Discussion

4.1. Geospatial variations in soil Hg

In this study, the concentrations of THg in soils collected from the BR1, BR2, BR3, BR4, and BR5 sites were approximately three times higher than the reference background level of 110 $ng\ g^{-1}$ THg in Guizhou Province, China (Tang et al., 2017). These data were also higher than those in other sites (BR6, BR7, and BR8); therefore, we consider that the BR1, BR2, BR3, BR4, and BR5 sites were Hg-impacted. The concentrations of THg in soils collected from BR6, BR7, and BR8 sites were close to the reference value. This suggests that these sites were slightly affected by mercury and sites such as BR6 site can be considered non-polluted.

According to the geographical location of the sites, the BR1, BR2, BR3, BR4, and BR5 sites with heavy Hg pollution are close to the pollution source (GOCP). However, the BR6, BR7, and BR8 sites are located in remote riparian zones close to GOCP. This suggests a decreasing trend of THg concentration along the riparian zones, with higher concentrations closer to the pollution source of Hg contaminants (GOCP). Similar findings were reported by other studies such as Qiu et al., 2005b, who observed higher concentrations of soil THg near an abandoned Hg mine than at other remote locations. Pant et al., 2011 also reported a decreasing trend in Hg concentrations along the riparian zones of a creek, where Hg was seriously contaminated by Hg discharged from the upstream energy department.

Hg in soil can accumulate over time in the presence of a continuous addition of Hg from adjacent polluted surface water (Jackson et al., 2019; Pant et al., 2011). Several studies have reported a decreasing trend of THg in surface water and sediments in deepwater and shoalwater areas along the Baihua Reservoir (Long et al., 2018; Zhang, 2016; Yan et al., 2008). Their findings concord with this study. It is suggested that the riparian zones closer to the GOCP are likely to be exposed to higher concentrations of Hg, giving rise to a decreasing trend of Hg along the riparian zones of Baihua Reservoir.

All sites were shown to have quantifiable MeHg. Several studies have considered concentrations of MeHg >1 $ng\ g^{-1}$, which is indicative of contaminated soils (Perez et al., 2019; Guedron et al., 2011; Feng et al., 1997). This value was lower than the MeHg concentrations in the BR1, BR2, BR3 and BR7 sites and therefore, these riparian zones can be considered as contaminated. Based on this reference value, we consider the BR4, BR5, BR6 and BR8 sites to be non-impacted.

The geospatial variation of MeHg along the riparian zones was similar to that of THg. The BR1, BR2, and BR3 sites are closer to the GOCP with their higher MeHg concentrations. The lowest concentrations of

Table 1
THg and MeHg concentrations (ng g^{-1}) in soils and vegetation, different letters (a to b) implicate significant differences (p < 0.05) among sampling areas.

Species		Plant part	BR1	BR2	BR3	BR4	BR5	BR6	BR7	BR8	Mean ± sd
Alternanthera philoxeroides	THg	Above	–	11.7	30.7	17.6	46.8	36.7	38.7	–	30.3 ± 13.3
		Below	–	12.4	35.9	19.0	35.2	23.6	23.8	–	25.0 ± 9.16
	MeHg	Above	–	0.36	0.28	0.57	0.32	0.23	0.30	–	0.34 ± 0.11
		Below	–	0.28	0.19	0.84	0.70	0.28	0.28	–	0.42 ± 0.26
Conyza Canadensis	THg	Above	33.9	–	79.1	–	43.9	57.4	63.2	–	55.4 ± 17.4
		Below	11.6	–	24.7	–	52.2	29.0	67.9	–	37.0 ± 22.5
	MeHg	Above	0.49	–	0.54	–	0.38	0.42	0.61	–	0.48 ± 0.09
		Below	0.41	–	1.14	–	0.25	0.32	0.20	–	0.46 ± 0.38
Crassocephalum crepidioides	THg	Above	69.9	81.6	53.7	–	93.7	–	–	–	74.7 ± 17.0
		Below	54.4	66.5	15.5	–	29.3	–	–	–	41.4 ± 23.2
	MeHg	Above	0.27	0.76	0.47	–	0.39	0.56	–	–	0.48 ± 0.18
		Below	0.16	0.52	0.42	–	0.13	0.49	–	–	0.34 ± 0.18
Cynodon dactylon	THg	Above	93.2	161	92.3	–	30.3	41.1	22.8	–	73.3 ± 52.5
		Below	21.9	94.2	26.6	–	39.0	72.3	35.4	–	48.2 ± 28.6
	MeHg	Above	0.48	0.75	0.24	–	0.35	1.06	0.28	–	0.52 ± 0.32
		Below	0.59	1.29	0.30	–	0.40	0.84	0.21	–	0.60 ± 0.40
Echinochloa crusgali	THg	Above	65.7	–	–	–	–	41.6	47.5	–	51.5 ± 12.5
		Below	28.0	–	–	–	–	39.7	22.5	–	30.0 ± 8.77
	MeHg	Above	0.30	–	–	–	–	0.42	0.50	–	0.40 ± 0.10
		Below	0.59	–	–	–	–	0.36	0.40	–	0.44 ± 0.12
Gnaphalium affine	THg	Above	52.9	106	–	–	–	39.5	–	–	66.1 ± 35.1
		Below	38.4	76.3	–	–	–	62.8	–	–	59.1 ± 19.2
	MeHg	Above	0.26	0.42	–	–	–	0.41	–	–	0.36 ± 0.09
		Below	0.16	1.37	–	–	–	0.57	–	–	0.69 ± 0.61
Hemarthria altissima	THg	Above	52.8	11.3	35.6	100	27.0	–	57.7	–	47.4 ± 30.9
		Below	37.6	12.5	25.6	69.5	34.9	–	67.6	–	41.2 ± 22.8
	MeHg	Above	0.38	0.26	0.28	0.45	0.35	–	0.47	–	0.36 ± 0.08
		Below	0.49	0.40	0.45	0.37	0.56	–	0.34	–	0.43 ± 0.08
Polygonum hydropiper	THg	Above	62.9	–	38.0	–	50.2	68.5	34.8	–	50.8 ± 14.8
		Below	11.8	–	55.7	–	193	56.6	37.4	–	70.9 ± 70.6
	MeHg	Above	0.37	–	0.26	–	0.26	0.43	0.36	–	0.33 ± 0.07
		Below	0.33	–	0.25	–	0.70	0.62	0.17	–	0.41 ± 0.23
Rumex japonicus	THg	Above	76.1	35.6	39.5	–	49.9	98.7	40.6	–	56.7 ± 25.2
		Below	83.2	33.9	144	–	30.4	20.9	33.6	–	57.7 ± 47.7
	MeHg	Above	0.49	0.59	0.31	–	0.35	0.70	0.40	–	0.47 ± 0.15
		Below	0.71	0.60	0.20	–	0.55	0.34	0.25	–	0.44 ± 0.20
Setaria viridis	THg	Above	25.4	–	39.4	–	38.5	–	–	–	34.4 ± 7.87
		Below	25.5	–	24.1	–	11.3	–	–	–	20.2 ± 7.78
	MeHg	Above	0.25	–	0.40	–	0.43	–	–	–	0.36 ± 0.09
		Below	0.26	–	0.27	–	0.29	–	–	–	0.27 ± 0.01
Solanum nigrum	THg	Above	–	–	50.9	–	161	–	40.3	–	84.1 ± 66.8
		Below	–	–	19.1	–	108	–	60.0	–	62.2 ± 44.2
	MeHg	Above	–	–	0.28	–	0.23	–	0.45	–	0.31 ± 0.11
		Below	–	–	1.51	–	0.49	–	0.68	–	0.89 ± 0.54
Soil sample	THg		304[a]	371[a]	323[a]	347[a]	340[a]	109[b]	128[b]	134[b]	
	MeHg		1.80[a]	1.00[a]	1.40[a]	0.56[a]	0.79[a]	0.61[a]	1.20[a]	0.32[a]	
Distance to GOCP (km)			11	12	13	13	14	14	16	18	
Soil organic matter (%)			7.50	7.10	8.70	3.80	3.70	6.40	6.00	3.60	

MeHg were found at the BR8 site which is the farthest from GOCP. The similar geospatial variation between THg and MeHg suggests that THg could influence the distribution of MeHg. Several studies have reported that soils with higher THg concentrations show higher MeHg levels due to more inorganic Hg used to methylate (Qiu et al., 2005b; Meng et al., 2014). In addition, MeHg showed a significant correlation with soil organic matter, which was in agreement with other report (Meng et al., 2016). This could be because organic matter provides nutrients for methylated microorganisms (Liang, 2013).

However, the sites of BR4 and BR5 showed higher soil THg concentrations, with no MeHg risks. The BR7 site with MeHg contamination showed high soil organic matter and low THg concentrations. These findings suggest that Hg methylation in the riparian zone is influenced by other factors such as physicochemical parameters, Hg availability, and biological activity (Yudovich and Ketris, 2005; Center, 2001; Carpi, 1997).

4.2. Mercury distribution in vegetation

The concentrations of THg in the vegetation studied were higher than those found in other areas with lower soil THg levels such as the riparian zones of the Three Gorges Reservoir in China (1.62 to 49.4 ng g^{-1}) (Liang et al., 2015), and Sanjiang Plain in China (23.1 to 82.5 ng g^{-1}) (Liu et al., 2004). However, the THg concentrations in vegetation growing at the Hg mine sites in Almaden and Badajoz in Spain (Fernandez-Martinez et al., 2015) and moss samples growing in Wanshan Hg mine districts in China (Qiu et al., 2005b) were significantly higher than those recorded in the current study. The MeHg concentrations in the vegetation studied here were higher than those reported in other unpolluted areas such as Lovca in Slovakia (0.02 to 0.06 ng g^{-1}) (Dombaiova, 2005), but lower than those reported in some mining districts such as Asturias in Spain (2.30–7.50 ng g^{-1}) (Fernandez-Martinez et al., 2015), and Guizhou in China (10.8 to 132 ng g^{-1}) (Meng et al., 2014). These comparisons suggest that the THg and MeHg in the vegetation studied here were at moderate concentrations and could be considered to be affected by Hg contamination.

The vegetation in this study had different morphological and physiological characteristics. These differences resulted in different concentrations of Hg accumulated in the vegetation. For example, *Solanum nigrum* showed high concentrations of THg and MeHg in its below ground portion. This plant species was found to have the potential for phytoremediation of contaminated soil and subsequently accumulated
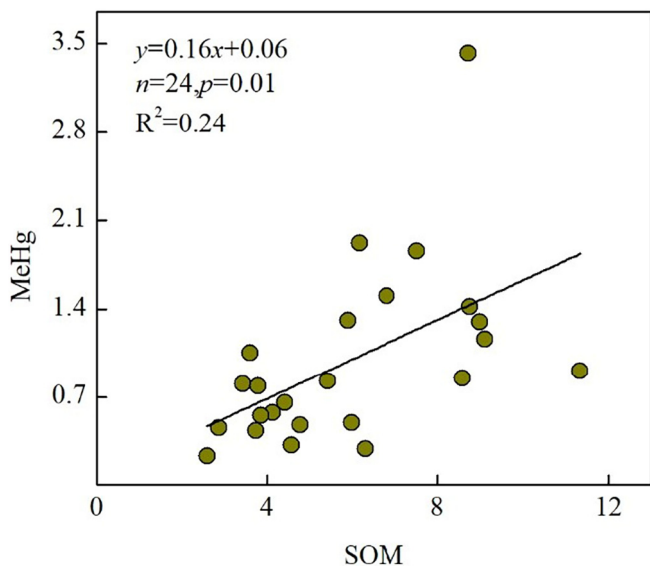
$y=0.16x+0.06$
$n=24, p=0.01$
$R^2=0.24$

Fig. 2. Correlation plots of MeHg vs. SOM in riparian soils.

high concentrations of Hg (Girdhar et al., 2014). Moreover, vegetation growing in soils with higher Hg concentrations exhibited higher Hg concentrations. This suggests that mercury accumulation depends not only on soil pollution, but also on the plants under consideration and their ability to incorporate it. Although the concentrations of THg in some plant species were high, they did not exceed that in the soils. Some species, however, had MeHg concentrations higher than those in the soils. This may be due to the bioconcentration characteristics of MeHg (Campbell et al., 2005; Kidd et al., 2012). For example, MeHg concentration in the below ground portion of *Cynodon dactylon* was higher than that in the soils. Liang et al. (2015) reported that this species had developed roots and therefore could accumulate more MeHg.

4.3. Potential for phytoextraction

In this study, we adopted BCF and TF to evaluate the accumulation and transfer of Hg in vegetation. The BCFs for the vegetation investigated were
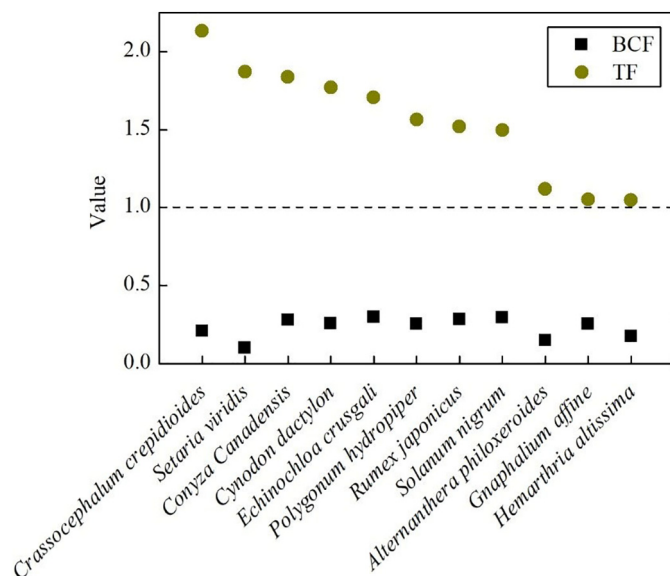

Fig. 3. BCF and TF for THg in vegetation.

low, and similar to the plants in the mining area of Almadén (0.004–0.49) (Millan et al., 2006; Moreno-Jimenez et al., 2006). The low BCF values are likely due to the THg concentrations of the riparian soils being mainly present in very insoluble forms as elemental Hg or matrix-bound Hg.

The TFs for the vegetation investigated were always higher than 1, a critical characteristic value associated with accumulator plants (Zhao et al., 2019; Baker et al., 1994). This may be due to soil Hg contamination, resulting in stress on the roots, which drove the Hg to translocate to the above ground plant portion to alleviate its stress on the roots. In general, vegetation with TF >1 has the potential for phytoextraction.

5. Conclusions

Compared to the reference values, the soils in the riparian zones close to the pollution source of Hg (GOCP) presented higher Hg contamination, with relatively light Hg contamination in remote areas.

We found a decreasing trend of THg concentrations along the riparian zones, with higher concentrations closer to the pollution source of Hg contaminants (GOCP). MeHg showed a significant correlation with soil organic matter.

The vegetation studied here can be considered to be impacted by Hg contamination. Different concentrations of total and methyl mercury were found among the different plant species. Higher Hg concentrations in the soils and higher Hg concentrations in the vegetation suggest that the mercury accumulation ability of riparian plants is affected by plant physiological characteristics and soil mercury concentrations.

Although the BCFs of the plants examined were low, their TFs were >1, which indicates their potential for phytoextraction in Hg-impacted riparian zones.

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CRediT authorship contribution statement

Qiuhua Li: Resources, Writing - review & editing, Supervision. **Li Tang:** Conceptualization, Methodology, Investigation, Writing - original draft, Visualization, Formal analysis. **Guangle Qiu:** Writing - review & editing, Supervision. **Chunhong Liu:** Writing - review & editing.

Declaration of interest statement

The authors declared that they have no conflicts of interest to this work.

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

References

Baker, A.J.M., Reeves, R.D., Hajar, A.S.M., 1994. Heavy metal accumulation and tolerance in British populations of the metallophyte *Thlaspi caerulescens* J. & C. Presl (Brassicaceae). New Phytol. 127 (1), 61–68. https://doi.org/10.1111/j.1469-8137.1994.tb04259.x.

Campbell, L.M., Norstrom, R.J., Hobson, K.A., Muir, D.C.G., Backus, S., Fisk, A.T., 2005. Mercury and other trace elements in a pelagic Arctic marine food web (Northwater Polynya, Baffin Bay). Sci. Total Environ. 351, 247–263. https://doi.org/10.1016/j.scitotenv.2005.02.043.

Carpi, A., 1997. Mercury from combustion sources: a review of the chemical species emitted and their transport in the atmosphere. Water Air Soil Pollut. 98 (3–4), 241–254. https://doi.org/10.1007/BF02047037.

Center, N.I., 2001. Proceedings of nimd forum 2001 mercury research: today and tomorrow. for M. D. M. Retrieved from. nimd.env.go.jp/english/kenkyu/nimd_forum/nimd_forum_2001.html.

Covelli, S., Faganeli, J., Horvat, M., Brambati, A., 2001. Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic sea). Appl. Geochem. 16 (5), 541–558. https://doi.org/10.1016/S0883-2927(00)00042-1.

Dombaiova, R., 2005. Mercury and methylmercury in plants from differently contaminated sites in Slovakia. Plant Soil Environ. 51 (10), 456–463. https://doi.org/10.17221/3617-PSE.

Driscoll, C.T., Han, Y.J., Chen, C.Y., Evers, D.C., Lambert, K.F., Holsen, T.M., Kamman, N.C., Munson, R.K., 2007. Mercury contamination in forest and freshwater ecosystems in the northeastern United States. Bioscience 57 (1), 17–28. https://doi.org/10.1641/B570106.

Du, H., Ma, M., Sun, T., Dai, X., Yang, C., Luo, F., Wang, D., Igarashi, Y., 2017. Mercury-methylating genes dsrB and hgcA in soils/sediments of the Three Gorges Reservoir. Environ. Sci. Pollut. Res. 24 (5), 5001–5011. https://doi.org/10.1007/s11356-016-8213-9.

Feng, X.B., Cai, Y.C., Zheng, W.G., 1997. The distribution of various mercury species in soil. Chin. J. Geochem. 16 (2), 183–188. https://doi.org/10.1007/BF02843398.

Feng, X.B., Sommar, J., Lindqvist, O., Hong, Y.T., 2002. Occurrence, emissions and deposition of mercury during coal combustion in the Province Guizhou, China. Water Air Soil Pollut. 139 (1–4), 311–324. https://doi.org/10.1023/a:1015846605651.

Feng, X.B., Yan, H.Y., Wang, S.F., Qiu, G.L., Tang, S.L., Shang, L.H., Dai, Q.J., Hou, Y.M., 2004. Gaseous mercury exchange rate between air and water over Baihua reservir, Guizhou, China. Atmos. Environ. 38 (28), 4721–4732. https://doi.org/10.1016/j.atmosenv.2004.05.023.

Feng, X.B., Foucher, D., Hintelmann, H., Yan, H.Y., He, T.R., Qiu, G.L., 2010. Tracing mercury contamination sources in sediments using mercury isotope compositions. Environ. Sci. Technol. 44, 3363–3368. https://doi.org/10.1021/es9039488.

Fernandez-Martinez, R., Larios, R., Gomez-Pinilla, I., Gomez-Mancebo, B., Lopez-Andres, S., Loredo, J., Ordonez, A., Rucandio, I., 2015. Mercury accumulation and speciation in plants and soils from abandoned cinnabar mines. Geoderma 253, 30–38. https://doi.org/10.1016/j.geoderma.2015.04.005.

Girdhar, M., Sharma, N.R., Rehman, H., Kumar, A., Mohan, A., 2014. Comparative assessment for hyperaccumulatory and phytoremediation capability of three wild weeds. Biotech 4 (6), 579–589. https://doi.org/10.1007/s13205-014-0194-0.

Guedron, S., Grimaldi, M., Grimaldi, C., Cossa, D., Tisserand, D., Charlet, L., 2011. Amazonian former gold mined soils as a source of methylmercury: evidence from a small scale watershed in French Guiana. Water Res. 45 (8), 2659–2669. https://doi.org/10.1016/j.watres.2011.02.022.

Hall, B.D., St Louis, V.L., Rolfhus, K.R., Bodaly, R.A., Beaty, K.G., Paterson, M.J., Cherewyk, K.A., 2005. Impacts of reservoir creation on the biogeochemical cycling of methyl mercury and total mercury in boreal Upland Forests. Ecosystems 8 (3), 248–266. https://doi.org/10.1007/s10021-003-0094-3.

He, T.R., Feng, X., Dai, Q.J., Qiu, G.L., Shang, L.H., Jiang, H., Liang, L., 2004. Determination of methyl mercury in sediments and soils by GC-CVAFS after aqueous phase ethylation. Earth Environ 32 (2), 83–86. https://doi.org/10.3969/j.issn.1672-9250.2004.02.016.

Jackson, A.K., Eagles-Smith, C.A., Emery, C., 2019. Spatial variation in aquatic invertebrate and riparian songbird mercury exposure across a river-reservoir system with a legacy of mercury contamination. Ecotoxicology, 1–10 https://doi.org/10.1007/s10646-019-02043-z.

Kidd, K.A., Muir, D.C.G., Evans, M.S., Wang, X., Whittle, M., Swanson, H.K., Johnston, T., Guildford, S., 2012. Biomagnification of mercury through lake trout (Salvelinus namaycush) food webs of lakes with different physical, chemical and biological characteristics. Sci. Total Environ. 438, 135–143. https://doi.org/10.1016/j.scitotenv.2012.08.057.

Kim, E., Kim, H., Shin, K.H., Kim, M.S., Kundu, S.R., Lee, B.G., Han, S., 2012. Biomagnification of mercury through the benthic food webs of a temperate estuary: Masan Bay, Korea. Environ. Toxicol. Chem. 31 (6), 1254–1263. https://doi.org/10.1002/etc.1809.

Lee, K.H., Isenhart, T.M., Schultz, R.C., Mickelson, S.K., 2000. Multispecies riparian buffers trap sediment and nutrients during rainfall simulations. J. Environ. Qual. 29 (4), 1200–1205. https://doi.org/10.2134/jeq2000.00472425002900040025x.

Li, Z.G., Feng, X.B., He, T.X., Yan, H.Y., Liang, L., 2005. Determination of total mercury in soil and sediment by aquaregia digestion in the water bath coupled with cold vapor atom fluorescence spectrometry. Bull. Mineral. Petrolo. Geochem. 24 (2), 140–143. https://doi.org/10.3969/j.issn.1007-2802.2005.02.009.

Li, R., Wu, H., Ding, J., Fu, W., Gan, L., Li, Y., 2017. Mercury pollution in vegetables, grains and soils from areas surrounding coal-fired power plants. Sci. Rep. 7. https://doi.org/10.1038/srep46545.

Liang, X.B., 2013. Mercury methylation bacteria and methyl mercury producing: a review. Chin. J. Ecol. 32 (3), 755–761 (CNKI:SUN:STXZ.0.2013-03-036).

Liang, L., Horvat, M., Bloom, N.S., 1994. An improved speciation method for mercury by GC/CVAFS after aqueous phase ethylation and room temperature precollection. Talanta 41 (3), 371–379. https://doi.org/10.1016/0039-9140(94)80141-X.

Liang, L.N., Jiang, G.B., Hu, J.T., 2001. Determination of inorganic mercury and total organomercury in chemical waste water by cold vapor generation-atomic fluorescence spectrometry. Chin. J. Anal. Chem. 49 (4), 403–405 in Chinese. https://doi.org/10.3321/j.issn:0253-3820.2001.04.008.

Liang, L., Wang, Y.M., Li, X.Y., Tang, Z.Y., Zhang, X., Zhang, C., Wang, D.Y., 2015. Distribution of mercury in plants at water-level-fluctuating zone in the three gorges reservoir. Environ. Sci. 36 (11), 4103–4111. https://doi.org/10.13227/j.hjkx.2015.11.021.

Liang, P., Feng, X., You, Q., Gao, X., Xu, J., Wong, M., Christie, P., Wu, S.C., 2017. The effects of aquaculture on mercury distribution, changing speciation, and bioaccumulation in a reservoir ecosystem. Environ. Sci. Pollut. Res. 24 (33), 25923–25932. https://doi.org/10.1007/s11356-017-0189-6.

Liu, R.H., Wang, Q.C., Liu, X.G., Li, Z.B., Wang, Y., 2004. Distribution and stock of mercury in typical wetland plant in the Sanjiang plain. Chin. J. Appl. Ecolo. 15 (2), 287–290. http://www.cjae.net/CN/Y2004/V/I2/287.

Long, S.X., Hamilton, P.B., Yang, Y., Wang, S., Huang, W.D., Chen, C., Tao, R., 2018. Differential bioaccumulation of mercury by zooplankton taxa in a mercury-contaminated reservoir Guizhou China. Environ. Pollut. 239, 147–160. https://doi.org/10.1016/j.envpol.2018.04.008.

Meng, M., Li, B., Shao, J.J., Wang, T., He, B., Shi, J.B., Ye, Z.H., Jiang, G.B., 2014. Accumulation of total mercury and methylmercury in rice plants collected from different mining areas in China. Environ. Pollut. 184 (1), 179–186. https://doi.org/10.1016/j.envpol.2013.08.030.

Meng, B., Feng, X., Qiu, G., Li, Z., Yao, H., Shang, L., Yan, H.Y., 2016. The impacts of organic matter on the distribution and methylation of mercury in a hydroelectric reservoir in Wujiang River, Southwest China. Environ. Toxicol. Chem. 35 (1), 191–199. https://doi.org/10.1002/etc.3181.

Mergler, D., Anderson, H.A., Chan, L.H.M., Mahaffey, K.R., Murray, M., Sakamoto, M., Stern, A.H., 2007. Methylmercury exposure and health effects in humans: a worldwide concern. Ambio 36 (1), 3–11. https://doi.org/10.1579/0044-7447(2007)36[3:MEAHEI]2.0.CO;2.

Millan, R., Gamarra, R., Schmid, T., Sierra, M.J., Quejido, A.J., Sanchez, Z.M., Cardona, A.I., Fernandez, M., Vera, R., 2006. Mercury content in vegetation and soils of the Almaden mining area (Spain). Sci. Total Environ. 368 (1), 79–87. https://doi.org/10.1016/j.scitotenv.2005.09.096.

Moreno-Jimenez, E., Gamarra, R., Carpena-Ruiz, R.O., Millan, R., Penalosa, J.M., Esteban, E., 2006. Mercury bioaccumulation and phytotoxicity in two wild plant species of Almaden area. Chemosphere 63 (11), 1969–1973. https://doi.org/10.1016/j.chemosphere.2005.09.043.

Pant, P., Allen, M., Tansel, B., 2011. Mercury contamination in the riparian zones along the East Fork Poplar Creek at Oak Ridge. Ecotox. Environ. Safe. 74 (3), 467–472. https://doi.org/10.1016/j.ecoenv.2010.10.009.

Perez, P.A., Hintelmann, H., Lobos, G., Bravo, M.A., 2019. Mercury and methylmercury levels in soils associated with coal-fired power plants in Central-Northern Chile. Chemosphere 237. https://doi.org/10.1016/j.chemosphere.2019.124535.

Qian, X., Xu, X., Wu, Y., Xu, Z., Meng, Q., Yang, C., Zhou, H., Qiu, G., 2019. Distribution of inorganic mercury and methylmercury in wild plants inhabited on abandoned lands of Wanshan hg mining region, Guizhou Province. Chin. J. Ecol. 38 (2), 558–566. https://doi.org/10.13292/j.1000-4890.201902.001.

Qiu, G.L., Feng, X.B., Liang, L., Shang, L.H., He, T.X., Yan, H.Y., Jiang, H., Wang, S., 2005a. Determination of methylmercury in moss by ethylation – gas chromatography-cold vapor atomic fluorescence spectrometry with solvent extraction. J. Instr. Anal. 24 (1), 29–32 (CNKI:SUN:TEST.0.2005-01-006).

Qiu, G.L., Feng, X.B., Wang, S.F., Shang, L.H., 2005b. Mercury and methylmercury in riparian soil, sediments, mine-waste calcines, and moss from abandoned Hg mines in east Guizhou province, southwestern China. Appl. Geochem. 20 (3), 627–638. https://doi.org/10.1016/j.apgeochem.2004.09.006.

Qiu, G., Feng, X., Wang, S., Shang, L., 2006. Environmental contamination of mercury from Hg-mining areas in Wuchuan, northeastern Guizhou, China. Environ. Pollut. 142 (3), 549–558. https://doi.org/10.1016/j.envpol.2005.10.015.

St Louis, V.L., Rudd, J.W.M., Kelly, C.A., Bodaly, R.A., Paterson, M.J., Beaty, K.G., Hesslein, R.H., Heyes, A., Majewski, A.R., 2004. The rise and fall of mercury methylation in an experimental reservoir. Environ. Sci. Technol. 38 (5), 1348–1358. https://doi.org/10.1021/es034424f.

Tang, L., Li, Q.H., Chen, C., Wang, L., He, Y., Chen, F.F., Gao, Y.C., Luo, L., 2017. Distribution and pollution characteristics of heavy metals in sediments of Puding Reservoir, Guizhou Province. Chin. Environ. Sci. 37 (12), 4710–4721. http://www.zghjkx.com.cn/CN/Y2017/V37/I12/4710.

Taylor, D.L., Linehan, J.C., Murray, D.W., Prell, W.L., 2012. Indicators of sediment and biotic mercury contamination in a southern New England estuary. Mar. Pollut. Bull. 64 (4), 807–819. https://doi.org/10.1016/j.marpolbul.2012.01.013.

Vidon, P., Allan, C., Burns, D., Duval, T.P., Gurwick, N., Inamdar, S., Lowrance, R., Okay, J., Scott, D., Sebestyen, S., 2010. Hot spots and hot moments in riparian zones: potential for improved water quality management. J. Am. Water Resour. Assoc. 46 (2), 278–298. https://doi.org/10.1111/j.1752-1688.2010.00420.x.

Witt, E.L., Kolka, R.K., Nater, E.A., Wickman, T.R., 2009. Influence of the forest canopy on Total and methyl mercury deposition in the boreal Forest. Water Air Soil Pollut. 199 (1–4), 3–11. https://doi.org/10.1007/s11270-008-9854-1.

Yan, H., Feng, X., Shang, L., Qiu, G., Dai, Q., Wang, S., Hou, Y., 2008. The variations of mercury in sediment profiles from a historically mercury-contaminated reservoir, Guizhou province, China. Sci. Total Environ. 407 (1), 497–506. https://doi.org/10.1016/j.scitotenv.2008.08.043.

Yudovich, Y.E., Ketris, M.P., 2005. Mercury in coal: a review part 2. Coal use and environmental problems. Int. J. Coal Geol. 62 (3), 135–165. https://doi.org/10.1016/j.coal.2004.11.003.

Zhang, Y., 2016. The Research of Mercury Pollution in Guizhou Baihua Lake and Analysy of Pollution Control Results. Taiyuan Univ Technol, China http://cdmd.cnki.com.cn/Article/CDMD-10112-1016714991.htm.

Zhao, L., Guo, Y., Meng, B., Yao, H., Feng, X., 2017. Effects of damming on the distribution and methylation of mercury in Wujiang River, Southwest China. Chemosphere 185, 780–788. https://doi.org/10.1016/j.chemosphere.2017.07.077.

Zhao, A., Gao, L., Chen, B., Feng, L., 2019. Phytoremediation potential of Miscanthus sinensis for mercury-polluted sites and its impacts on soil microbial community. Environ. Sci. Pollut. Res. 26, 34818–34829. https://doi.org/10.1007/s11356-019-06563-3.

Zheng, W., Feng, X.B., Li, G.H., Li, Z.G., 2006. Determination of total mercury in plants by HNO3 digestion in the water bath coupled with cold vapor atomic fluorescence spectrometry. Bull. Mineral. Petrolo. Geochem. 25 (3), 285–287. https://doi.org/10.3969/j.issn.1007-2802.2006.03.012.