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Weir building: a potential cost-effective method for reducing mercury leaching from abandoned mining tailings

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Highlights:

- A weir is tested on contaminated stream to reduce Hg transport to downstream.
- A whole year monitoring of Hg species was done at the inlet and outlet of the weir.
- Approximately 40.4% THg and 38.4% TMeHg was retained by the weir on annual basis.
- Intensive sampling at a rainstorm confirms the dominant role of particulate Hg.
- Weir construction is cost-effective to control particulate Hg transport.

Abstract

To mitigate mercury (Hg) pollution and reduce Hg transportation downstream, a weir was designed across a river system impacted by leachate from the slagheap of the Yanwuping Hg mine in Wanshan Hg mining area. A whole year monitoring of Hg species was conducted, and the efficiency of Hg reduction by the weir application was evaluated. The Hg concentrations in river water were significantly higher during the wet season than during the dry season. Waterflow was confirmed to be the main driving factor for Hg mobilization and transportation, and an episode study revealed that most Hg was released during storms. Increased monitoring and preventive maintenance work should be performed on barriers in advance of storms. A large fraction of total Hg (THg) and methylmercury (MeHg) is associated to particles. During the study period, approximately 412 g THg and 4.04 g total MeHg (TMeHg) were released from the YMM slagheap, of which 167 g THg and 1.15 g TMeHg were retained by the weir. Annually, 40.4% THg and 38.4% TMeHg was retained by the weir. Weir construction is considered as a potential cost-effective measure to mitigate Hg in river water and should be promoted and extended in the future after optimization.

Keywords: Stream water mercury speciation; weir construction; mercury retention; cost benefit analysis

1 Introduction

Mercury (Hg) is a biologically non-essential and highly toxic metal. Specifically, methyl mercury (MeHg) is of great concern due to its neurotoxicity [1] and effective biomagnification through the food chain [2, 3]. The global cycling of Hg perpetuated through atmospheric transport results in elevated Hg levels in fish of pristine aquatic ecosystems far from major source regions [4].

An abandoned Hg mining district is a significant source of Hg, and pose a continuous threat to local ecosystems [5-8]. Drainage from slagheaps is an important pathway introducing Hg to adjacent river systems via the discharge of Hg-bearing particles and dissolved Hg [9, 10]. Due to large amounts of Hg-containing secondary minerals in slagheap, such as elemental mercury, meta-cinnabar and mercury sulfate, chloride, and oxide compounds [11], Hg mine drainage zone may involve an active Hg methylation process [12]. River water with elevated Hg could cause high Hg levels in fish, crops, and vegetables [13, 14]. Both humans and wildlife are exposed to high total Hg (THg) and MeHg via food consumption [15, 16]. Meanwhile, Hg-bound particles can be transported hundreds of kilometers downstream [17]. Therefore, river systems heavily contaminated by Hg have become a major pathway for the downstream transport of Hg [18, 19]. After being contaminated by Hg, it may take long time, even centuries, to remediate river systems and attain more moderate Hg levels [5].

Isolation and containment, mechanical separation, pyro-metallurgical separation, chemical treatment, and permeable treatment walls are usually applied as prevention and remediation technologies in engineering practices [20]. The site characteristics are the basis for selection of appropriate prevention and remediation methods. As the third largest Hg mine in the world, Wanshan Hg mine has produced large amounts of Hg. More than 125 million tons of waste remains in Wanshan Hg mining areas [21]. THg and total MeHg (TMeHg) in river water near slagheaps can be as high as 12,000 ng/L and 11 ng/L, respectively [22, 23]. It may result in the Hg contamination of sediments in drinking water reservoirs along the Yangtze River. Therefore, appropriate and cost-effective environmental remediation measures should be implemented in Wanshan Hg mine. In Wanshan Hg mining area, the Hg concentrations in river water increase sharply with an increase of waterflow, and particulate Hg is the major component of THg [24]. Thus, source confinement by an

isolation and containment method has been implemented to prevent solid waste migration. However, although a slagheap has been covered with cement, mobilization of Hg often occurs due to penetration of constant runoff from upstream [7]. It is necessary to take measures to limit its impact in specific areas by building infrastructure.

Weir building was selected to retain Hg in the river due to its low-cost and low environmental impact. Weir can alter the flow characteristics of the water [25]. It includes a small dam across the horizontal width of a river. Weirs are constructed for varieties of purposes such as flow measurement [26], invasive species control [27], flood control [25]. Most other remediation technologies are energy-intensive, demanding high reagent consumption, or involving expensive maintenance costs [28], while a weir is supposed to be a cost-effective method to reduce fluvial particulate pollutants. Few studies about Hg remediation in river systems were applied at Hg-contaminated sites [29].

A weir was designed and constructed in Wanshan Hg mining area as a pilot study. Subsequently, hydrological parameters and Hg speciation in the river water up and downstream of the weir were measured biweekly over a full year period. The objectives of this study were to investigate the treatment efficiency of the weir after the cement coverage of slagheap and its influence factors of Hg retention by weir construction, to evaluate the cost and benefit of weir construction.

2 Materials and methods

2.1 Study area

Wanshan Hg mining area is located in Guizhou province, Southwest China. The Yanwuping mercury mine (YMM) is one of the largest Hg mines in Wanshan. The YMM covers approximately 1 km², with approximately 3.1*10⁵ m³ slag waste produced during the long time mining activities. In 2011, the slagheap was covered with cement. The YMM is located in a typical mountainous and karstic terrain, with elevations ranging from 340 to 1010 m.-The average annual rainfall is 1386 mm. The dominant ore mineral of the YMM is cinnabar [30]. More information about the YMM slagheap is present in SI.

Wengman River belongs to Yangtze River basin, originated from the YMM slagheap (Fig 1). The average water depth is typically 1 m in summer. Most Hg mine wastes and retorts in this region are located in scattered hillsides at the upstream

portion of the Wengman River.

2.2 Weir design

Using technical information from previous studies [7, 31], a concrete weir was built across the upstream portion of the Wengman River in February 2012. A weir trough was designed to determine the flow rate of water, with a flow measurement instrument employed. The location of the weir is approximately 1,000 m from the YMM slagheap. The width and height of the weir are 7 m and 1 m, respectively. A sketch of the weir design is supplied in SI.

2.3 Sampling

The flow measurement and sampling campaigns were conducted for a whole year. Water samples were collected biweekly from April 2012 to March 2013. The sampling sites are illustrated in Fig. 1.

Surface water samples were collected in duplicate at every sampling. One unfiltered sample was directly stored in a 200 mL borosilicate glass bottle for THg and TMeHg measurements, and the other sample was filtered *in situ* through a 0.45 μm polyvinylidene fluoride filter for dissolved Hg (DHg) and dissolved MeHg (DMeHg) analysis [18]. In addition, a 1.5 L sample was each time collected for the determination of total suspended solids (TSS) in water.

The sampling equipment, including filtration equipment and borosilicate glass bottles, were rinsed three times with river water. Both unfiltered and filtered samples were acidified by adding 0.4% (v/v) of ultra-pure HCl within 24 h of collection. The sample bottles were tightly sealed, placed in double plastic bags and stored in a clean container before analysis. Sampling, storage and preservation were conducted strictly according to USEPA Method 1631 [32].

A few flooding events occurred during summer 2012 and were unfortunately not captured by the discontinuous Hg sampling scheme. To elucidate the flooding effect, an intensive sampling campaign was instead performed during a rainstorm event in August 2013. The sampling was conducted every 5 minutes and lasted for a total of 1.7 hours.

2.4 Hg and MeHg analysis

Mercury fractions were operationally defined as THg, DHg, particulate Hg (PHg), TMeHg, DMeHg, and particulate MeHg (PMeHg) in the water samples [33]. Measurements of THg and DHg involved BrCl oxidation and SnCl₂ reduction,

pre-concentration and thermal reduction to Hg^0 by the dual stage Au amalgamation method and detection using a Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS, Model III, Brooks Rand, USA) following Method 1631 [32]. For MeHg, the water sample was distilled, ethylated, and enriched onto Tenax tubes, and TMeHg and DMeHg were measured following Method 1630 [34].

PHg and PMeHg were obtained as the difference between THg and TMeHg in filtered and unfiltered water, respectively [33, 35].

The ratio of PHg or DHg in THg were expressed as PHg% and DHg%, respectively. The ratio of PMeHg or DMeHg in TMeHg were expressed as PMeHg% and DMeHg%, respectively.

2.5 Hydrological parameters

Hydrological parameters of water temperature, pH, total dissolved solids (TDS), anions, cations, and dissolved organic carbon (DOC) were measured at each sampling campaign. Total suspended solids were obtained by weighing the filter after water samples was filtered. Detailed information for all experimental procedures is given in the SI.

2.6 Calculations and data analysis

The net retention flux of THg and TMeHg (hereafter: Net THg flux and Net TMeHg Flux, respectively) in river water was calculated using equation (1), and the Hg stock was calculated according to equation (2). Assuming the input and output water volume are equal, the retention ratio can be obtained according to equation (3).

$$\text{Net Hg Flux} = \sum V_{\text{water}} * (C_{\text{input}} - C_{\text{output}}) \quad (1)$$

$$\text{THg (or DHg) stock} = C_{\text{THg or DHg}} * \rho_{\text{slagheap}} * V_{\text{slagheap}} \quad (2)$$

$$\text{Retention ratio} = \frac{C_{\text{Input}} - C_{\text{Output}}}{C_{\text{Input}}} \times 100\% \quad (3)$$

where

C_{input} = input THg or TMeHg concentration;

C_{output} = output THg or TMeHg concentration;

V_{water} = water volume during a certain time.

Following the Chinese national standard (GB/T 2413-2413), the average bulk density (ρ_{slagheap}) of slag waste is estimated at $2.6 \times 10^3 \text{ kg/m}^3$. In turn, the total solid volume of the YMM slagheap (V_{slagheap}) is approximately $3.1 \times 10^5 \text{ m}^3$ [7].

All data analysis was performed using Microsoft Excel 2010 and SPSS 22, and all figures were created by Origin 9 software.

3 Results and discussion

3.1 Annual Hg speciation and efficiency of Hg retention

3.1.1 Relationships between Hg fractions and other parameters

TMeHg was significantly anti-correlated with pH (Table 1, two tailed ANOVA, $p < 0.01$). High pH could increase volatilization losses of elemental Hg from solution, leading to substrate reduction and decrease Hg methylation [36]. In turn, low pH can increase the solubility of MeHg and other forms of Hg in the environment; thus, the concentration of MeHg will increase in water [37].

Furthermore, TMeHg is significantly positively correlated with TSS. The correlation was even more manifest between PHg and TSS ($r = 0.86$, $p < 0.01$), implying that most Hg was in particulate state [31]. The negative correlation between SO_4^{2-} and different MeHg speciation ($r = -0.56$, $p < 0.01$) may suggest a lack of stable conditions for Hg methylation by sulfate reducing bacteria [38].

Positive correlations were found between Hg speciation and Ca^{2+} ($r > 0.30$, $p < 0.05$). Ca^{2+} is mainly from the local bedrock limestone, and limestone is associated with Hg ore [22]. After smelting of Hg ore, slaked lime and Hg residue was left in the Hg slag. The correlation between Hg fraction and Ca^{2+} in the slagheap upstream is of similar magnitude (Table S2, two tailed, $r > 0.3$, $p < 0.05$) [39].

3.1.2 Annual Hg speciation

Fig. 2 shows the time-concentration series of various Hg fractions measured at the three river sampling sites over a full year. During the sampling period, the mean THg values at input, internal, and output sites were $127 \pm 199 \text{ ng/L}$, $88.3 \pm 8.27 \text{ ng/L}$, $81.8 \pm 161 \text{ ng/L}$, respectively (Fig. 3). For PHg% (PHg/THg ratio), the input, internal, and output ratios were 76.8%, 73.6%, and 67.8%, respectively. The input, internal, and output PMeHg% were 57.6%, 52.3%, and 52.3%, respectively. According to the Hg data in water, during the sampling period, PHg was the dominant Hg fraction and MeHg mainly occurred as PMeHg.

TMeHg concentrations had significantly positive correlations with DMeHg and PMeHg (two tailed ANOVA, $p < 0.01$) (**Table S1**), suggesting that they had the same origin. The correlation between TMeHg and PMeHg was improved than that obtained between TMeHg and DMeHg, indicating that most of MeHg existed bound to particulates [22]. Significant correlations ($p < 0.01$) were found among different Hg speciation (**Table S2**), which confirmed that they had the same source.

3.1.3 Annual efficiency of Hg retention

Compared with THg at the input site, the THg level at the internal and the output site was significantly lower, especially at the output site (two-tailed paired t-test, $p < 0.01$). DHg at input site was higher than the DHg at the internal and the output site, especially at the internal site (two-tailed paired t-test, $p < 0.05$). The PHg at the input site was significantly higher than the PHg at the internal and the output site (two-tailed paired t-test, $p < 0.05$). For TMeHg, TMeHg at the output site was approximately 30% less than TMeHg at the input site. The DMeHg at the output site was significantly less than the DMeHg at the input site (two-tailed paired t-test, $p < 0.05$). The PMeHg at the output site was approximately 36% less than the PMeHg at the input site. In general, lower Hg in water can be found after the weir than before the weir.

The data indicate that a part of the particulate Hg was held back by the weir. For example, PHg and PMeHg were reduced by 43% and 36%, respectively, suggesting the effect of the weir. When the water flows through the weir, the suspended particles tend to settle with the slow water flow and long retention time [20].

3.2 Seasonal variations in Hg and MeHg fraction level and efficiency of Hg retention

3.2.1 Seasonal Hg and MeHg fraction patterns

Seasonal patterns were manifest for the various Hg and MeHg fractions (**Fig. 2**). At the three sites, all of the Hg fraction concentrations followed the order of wet season > normal season > dry season (**Fig. 4**). Both THg and DHg in the wet season were significantly higher than those in the dry season (two-tailed ANOVA, $p < 0.05$). peaking THg (767 ng/L), DHg (107 ng/L), and PHg (660 ng/L) concentrations were measured in the wet season. At the input site, the PHg in the wet season was significantly higher than in the dry season (ANOVA, $p < 0.05$). PHg% at the input and

output sites decreased from 79.8% to 71.6%, from 75.5% to 67% and from 41% to 29% for the wet season, normal season, and dry season, respectively.

For all three sites, the TMeHg, DMeHg, and PMeHg in the wet season were markedly higher than those in the dry season (two-tailed ANOVA, $p < 0.05$). At the three sites, TMeHg in the wet season can be 6-8 times higher than in the dry season, 3-6 times higher for DMeHg, and 11-16 times for PMeHg. The highest TMeHg (8.70 ng/L), DMeHg (2.11 ng/L), and PMeHg (6.65 ng/L) were obtained in the wet season. PMeHg% of input and output decreased from 61.5% to 57.8% in the wet season, from 53.8% to 40.8% in the normal season, and from 40.5% to 36.4% in the dry season.

In wet season, high fluvial Hg derived from the runoff from slagheap and catchment. In turn, high Hg input from slagheap and the erosion of elevated Hg soil into the river was mainly triggered by heavy precipitation events [40]. Moreover, resuspension of Hg buried in sediment is an additional potential source, which was induced by frequent rainfall and high waterflow [3, 41]. For TMeHg, the average concentrations in the normal and wet seasons were several times higher than that in the dry season, which may derive from active Hg methylation processes during the summer [42].

3.2.2 Seasonal variations in Hg retention efficiency

According to the paired THg concentration measurements at the input and output site, THg was significantly reduced by the weir, especially in the normal and dry seasons ($p < 0.01$). On an average, THg at the output site was 34.6%, 46% and 22.8% less than the THg at the input site in the wet season, normal season and dry season, respectively. Concerning PHg, the retention efficiency in the wet, normal, and dry seasons was 41.3%, 52%, and 48.9%, respectively, and decreased significantly in the normal and dry seasons (two-tailed paired T test, $p < 0.01$). The highest THg, and PHg removal efficiencies were obtained in the normal season. This can be explained by stationary flow conditions during the normal season (Fig. S3). On the contrary, in the wet season, waters upstream the weir were frequently turbid plausibly with resuspended Hg-rich particles [31]. The lowest THg removal efficiency in the dry season may due to the low initial THg in water and low particles containing in water [43].

The removal efficiency of TMeHg, PMeHg during the sampling period followed this order: normal season > wet season > dry season. TMeHg and PMeHg at the

output site were lower than those obtained at the input site. On an average, TMeHg at the output site was 28.6%, 42.4%, 10.8%, less than the TMeHg at the input site in the wet season, normal season, and dry season, respectively. The PMeHg at the output site was 32.8%, 56.3% and 20% less than the PMeHg at the input site in wet season, normal season, and dry season, respectively. In general, the weir can prevent MeHg from being transported downstream. That both the TMeHg and PMeHg concentrations decreased sharply may demonstrate the removal mechanism of the weir that the weir had the better efficiencies in retaining particles bond state than dissolved state [44]. The PMeHg% during the sampling time showed a downward trend, which may have occurred because the particle-bound MeHg was blocked by the weir and deposited [45]. However, in some cases (**Fig. 2**), the output TMeHg was slightly higher than the input TMeHg, which may be explained by episodic re-suspension of sedimentary particles caused by heavy rain [46], and may also imply on-going Hg methylation in the weir, both of which will contribute to the higher output TMeHg [47].

3.2.3 Waterflow-the driving factor of Hg transportation downstream

Waterflow was significantly linearly correlated with the precipitation ($r^2=0.70$, $p<0.001$) (**Fig. S2**), suggesting that the Wengman River is a seasonal river dominated by rainfall. Both the THg and TMeHg concentrations were significantly correlated with waterflow ($r=0.68$, $p<0.05$; $r=0.615$, $p<0.05$) (**Table S3**), indicating that precipitation-driven high waterflow is the main factor facilitating mobilization and transportation of THg and TMeHg downstream. THg concentration had a significantly positive relation with PHg ($r=0.99$, $p<0.01$), meanwhile there also existed a significantly positive relation between TMeHg and its particulate state - PMeHg ($r=0.98$, $p<0.01$) (**Table S2**). Combined with high particulate ratios, these positive relations indicated particulate bonded Hg play a dominant role in Hg transportation. Consequently, efficient control of Hg in particulate state is the key way to mitigate for downstream Hg transportation [7].

Waterflow was the driving factor of Hg transportation, and as mentioned above, most Hg was transported downstream during the wet season. Specifically, responses in fluvial Hg load to events of extreme rainfall must be examined in more detail (See Section 3.3).

3.3 Rainstorm case study

Fig. 5a, b illustrates the temporal trends of THg, waterflow and TSS following a rainstorm. At peaking waterflow, both THg and TSS displayed an increase by roughly four orders of magnitude compared to normal flow and were during the event highly correlated ($p < 0.0001$) (**Table S4**). Their correlation with waterflow was weaker ($0.68 < r < 0.77$) but still significant at $p < 0.05$.

During the rainstorm episode, PHg% increased dramatically to 99% (**Table S4**), which confirmed that TSS and THg originated from the same source. The observed magnitude of THg fluxes during the event indicates considerably quantities of Hg-bound particles being washed from the slagheap and then being re-suspended once they were released into the riverbed [41]. Such high TSS and Hg in river also alarm us to strengthen daily monitoring and maintenance work of both the dam of slagheap and the weir in case of dam break or massive leaks.

3.4 Economic cost analysis

Based on the daily average waterflow and the regression equation between waterflow and THg concentration, annual loadings of Hg were estimated.

3.4.1 THg and TMeHg balance

To evaluate the mass removal efficiency and the fate of Hg, a mass balance for THg and TMeHg was established for each season (**Table S1**). 94% of the annual THg input occurred during the wet season (June – August) with only minor contributions during the normal and dry seasons (4.4% and 1.7%, respectively). The net retention of THg flux by the weir in the wet, normal, and dry season was calculated to 159 g, 5.9 g, and 1.7 g corresponding to a mean THg mass removal efficiency of 40.4%. The TMeHg input followed a similar seasonal pattern as THg with 89% of the annual input during the wet season. On an average, the TMeHg mass removal efficiency (28.4%) was lower than for THg.

3.4.2 Cost-effectiveness analysis

The THg and DHg concentrations in the YMM slagheap were analyzed to evaluate the THg and DHg stock. The average THg concentration in slag was 23 mg/kg (range 13 - 41 mg/kg) (**Table S5**). The average concentration of DHg was 6.9 $\mu\text{g}/\text{kg}$ (range 3.6-12 $\mu\text{g}/\text{kg}$). Using Eq. 2 in Section 2.6, the THg and DHg stocks were calculated to 1,900 kg and 560 g, respectively.

In Hg polluted sites, monetary costs of removing 1 kg Hg from an aquatic environment are estimated in a range of approximately 2,500 - 1,100,000 USD [48]. In this study, the cost to construct and deploy the weir amounted to 3,170 USD and it was designed to be in service for at least 5 years. Expenses for dredging were taken into consideration, and the annual cost was estimated at 400 USD. During five years operation, the weir in the present study was estimated to retain approximately 833 g THg. Consequently, premised on our findings and predicted remediation costs globally [48], weir building stands out as a cost-effective method to reduce leaching and fluvial transport of Hg from mining tailings.

In the Wanshan Hg mining areas, more than 125 million tons of slag are piled along the river banks or in upstream areas [21]. The average THg in calcines was 48.4 mg/kg (range 0.6-267 mg/kg) with an average DHg/THg ratio of 0.058% [24]. Using Eq. 2, a total stock of approximately 6,050 tons of THg and 3.5 tons of DHg was present in this area. With the cement coverage of the slagheap, the major Hg emission of pollutants will change from THg (6,050 tons) to DHg (3.5 tons); together with the weir construction technology applied, the loadings of Hg into the river from slagheaps in this area will be significantly decreased at a low cost. Similarly, if wire construction technology can be applied worldwide in Hg mining areas, such as the Nevada Hg mines (Dutch Flat: 300 m³; Goldbanks: 10,000 m³; McDermitt: 1,000,000 m³) [49], Alaska Hg mines (Red Devil: 40,000 m³ [50]; Cinnabar Creek: 10,000 m³) [51], Terlingua Hg mine (>2,000,000 m³), Mariscal Hg mine (30,000 m³) [52], Almadén Hg mine (1,000,000 m³) [53], it would contribute significantly to the reduction of Hg in aquatic ecosystems around the world.

4 Conclusions

This pilot study evinced weirs to be a cost-effective way of retaining Hg mainly associated with particles from stream water impacted by leachate from Hg mining tailings. Annually, approximately 167 g THg and 1.2 g TMeHg were removed by the weir building while 245 g THg and 2.9 g TMeHg were transported further downstream. Associated with the low cost of 6200 USD to remove 1 kg Hg from streamwater, the systematic deployment of optimized weirs in river catchments of a Hg mining area has premises to mitigate for Hg pollution transported by surface water.

To increase the Hg removal capacity of the weir, the addition of absorptive materials, biofilm, or plants such as moss can be considered in the future. Long-term monitoring should be conducted to establish the baseline conditions and to document the effectiveness of remediation as it proceeds. It is necessary to take some special measures during rainstorm events.

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Figures

Fig. 1 Sampling sites description.

Fig. 2 Different Hg speciation at different sites during sampling period.

Fig. 3 Concentrations of different Hg speciation in different sampling points.

Fig. 4 Seasonal variations in Hg speciation.

Fig. 5 THg, TSS, and waterflow variation with time during a rainstorm event.

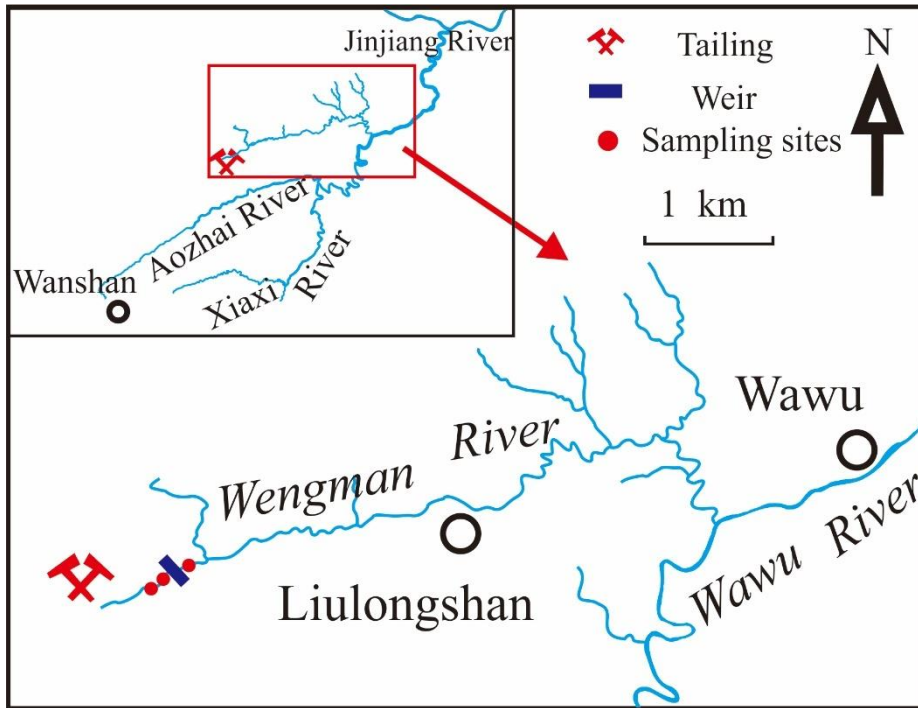


Fig. 1 Map of sampling locations

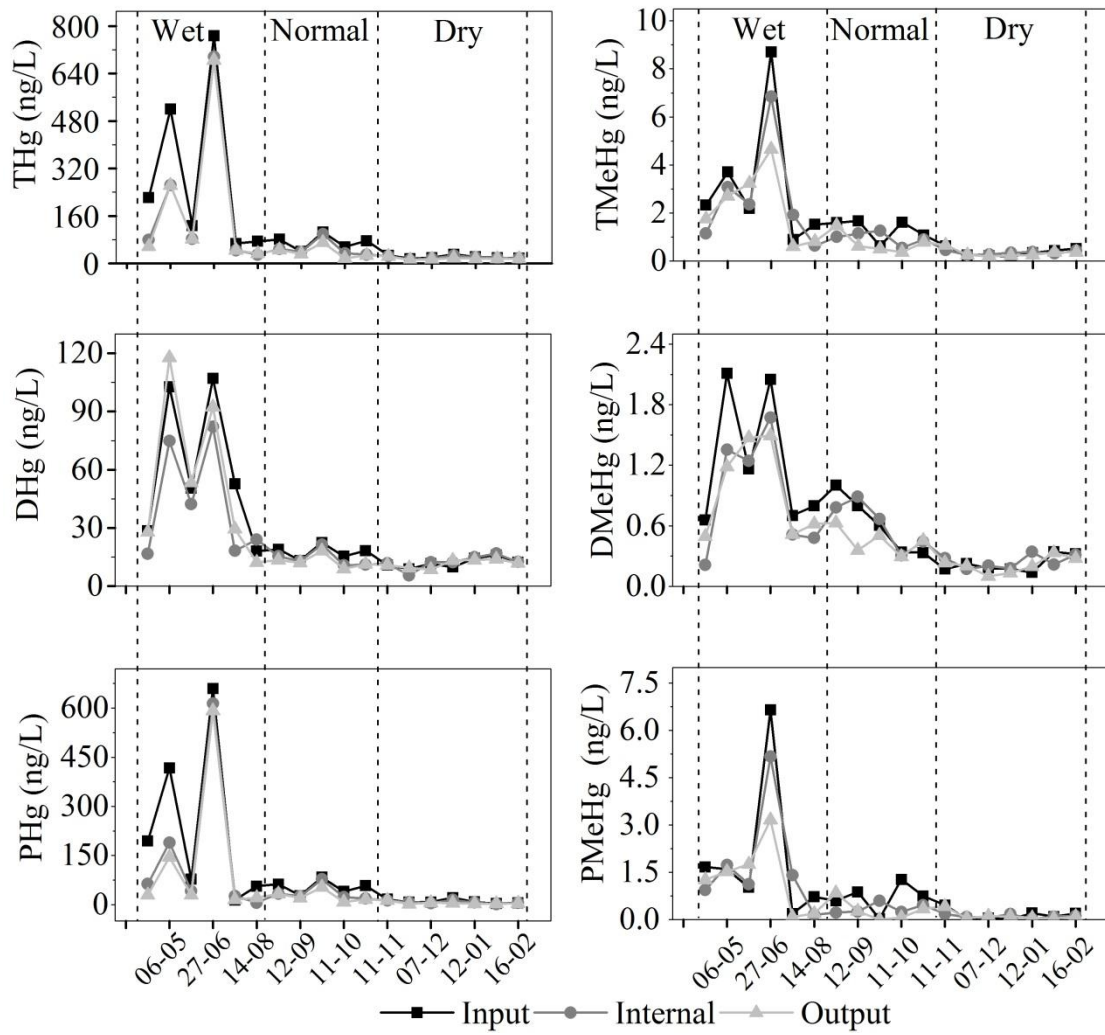


Fig. 2 Concentration-time series of measured Hg and MeHg fractions at the various sites during sampling period.

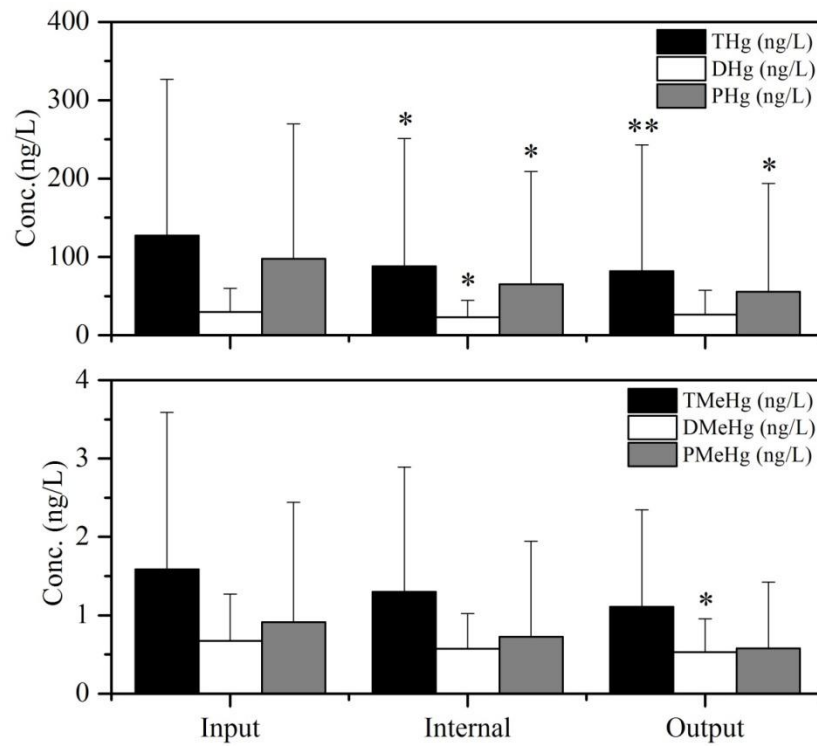


Fig. 3 Concentrations of different Hg speciation in different sampling points. * and ** represent significant differences compared with input site.

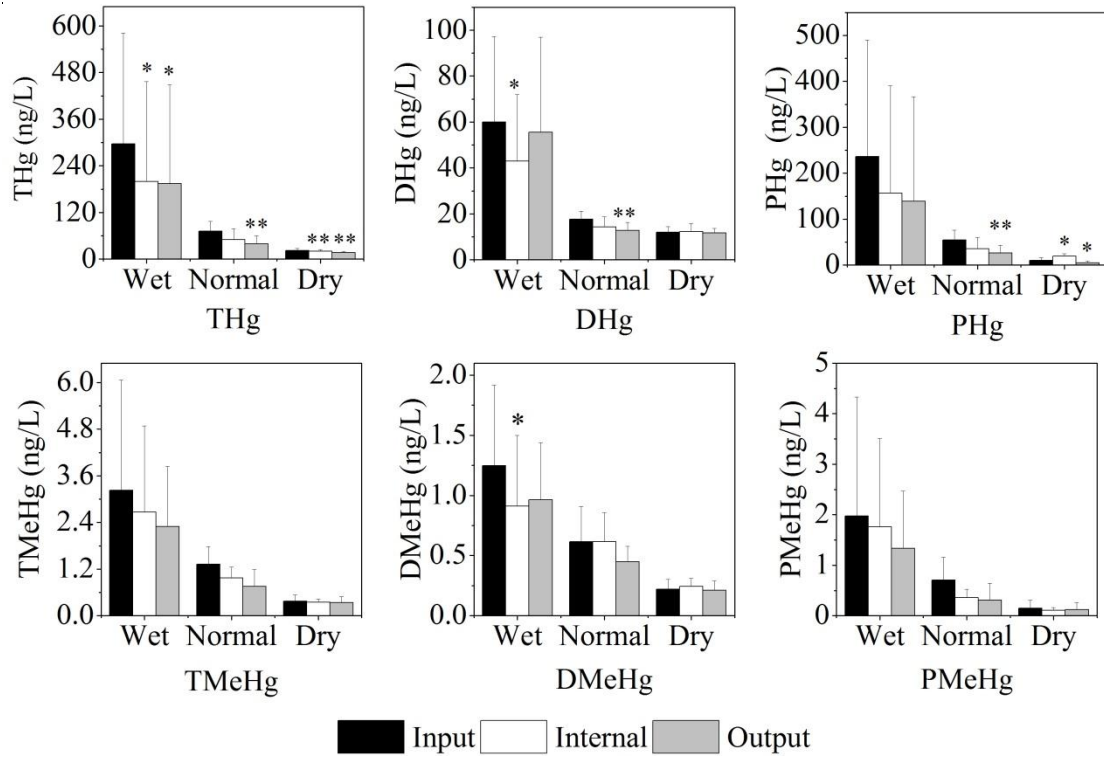


Fig. 4 Different Hg speciation in different seasons.

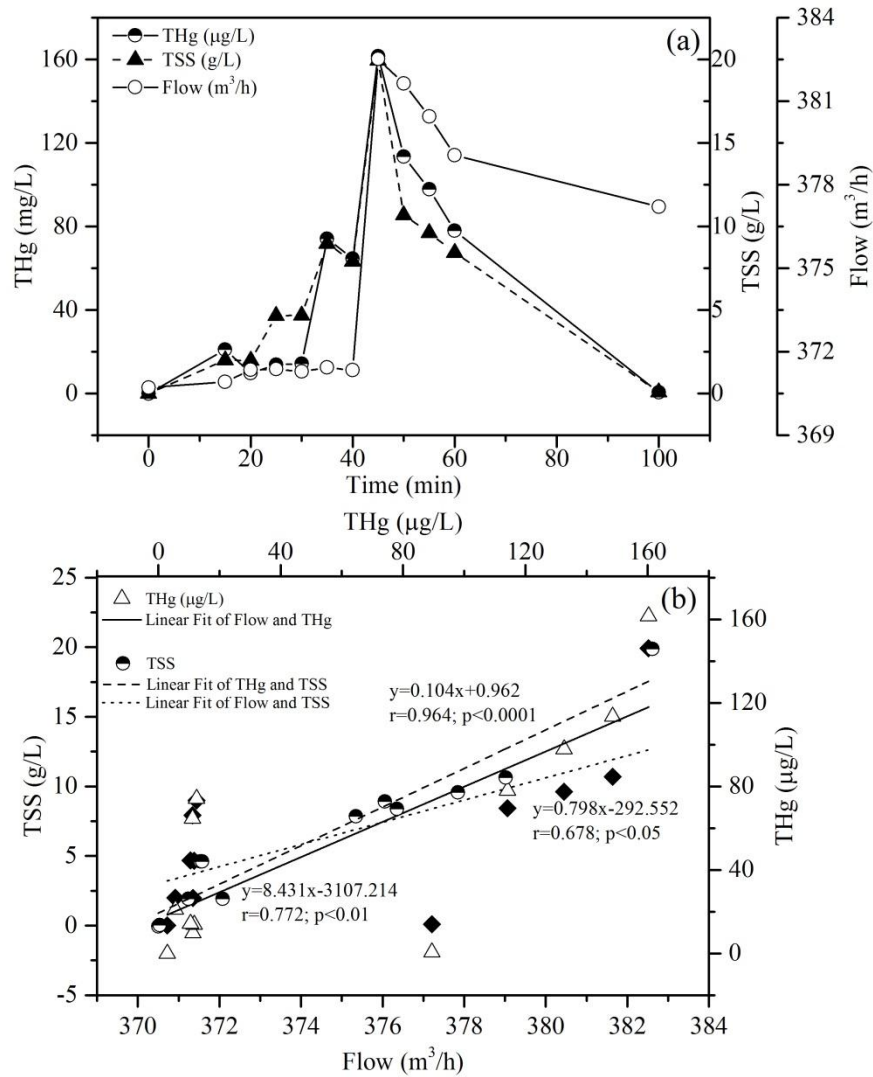


Fig. 5 THg, TSS, and waterflow variation with time during a rainstorm event.

1 **Tables**

2 **Table 1** Correlations between MeHg and the other factors.

3 **Table 2** Hg loads and removal efficiency.

4

5 **Table 1 Correlations between MeHg and the other factors.**

	TMeHg	DMeHg	PMeHg	pH	TDS	T
TMeHg	1.00					
DMeHg	0.880**	1.00				
PMeHg	0.970**	0.770**	1.00			
pH	-0.430**	-0.410**	-0.420**	1.00		
TDS	0.710**	0.700**	0.690**	-0.640**	1.00	
T	0.050	0.050	0.040	-0.010	0.090	1.00

6 TDS represents total dissolved solids, T represents temperature.

7 *. Significant correlation at 0.05 level (double side)

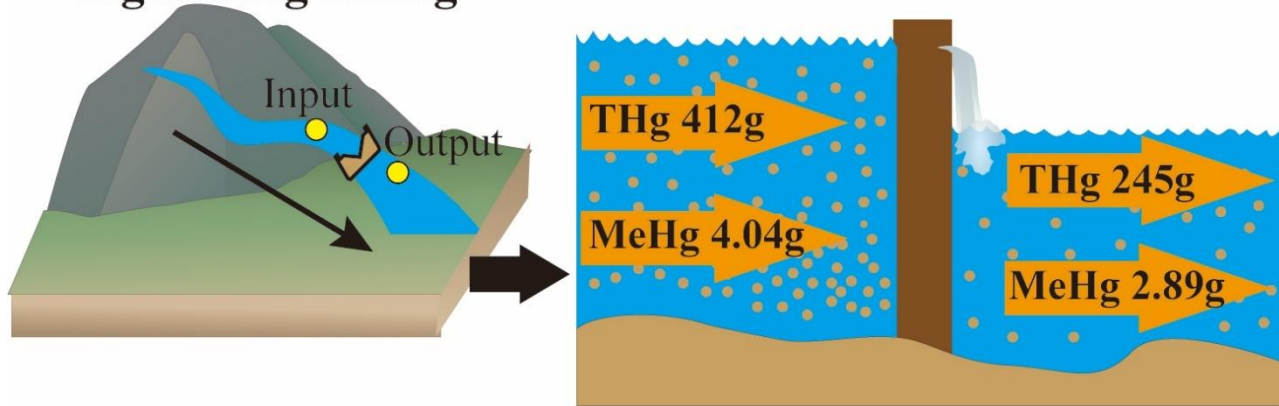
8 **. Significant correlation at 0.01 level (double side)

Table 2 Hg loads and removal efficiency.

Seasons	THg				MeHg			
	Input (g)	Output (g)	Net removal flux(g)	Mass removal efficiency (%)	Input (g)	Output (g)	Net removal flux (g)	Mass removal efficiency (%)
Wet	387	228	159	41.1%	3.60	2.61	0.990	27.5%
Normal	18.0	12.1	5.90	32.8%	0.320	0.180	0.140	43.3%
Dry	7.02	5.33	1.68	24%	0.120	0.110	0.0100	9.45%
Total amount	412	245	167	40.4%	4.04	2.89	1.140	35.8%

Graphical Abstract:

Hg mining tailing



Statement of novelty

In order to find solutions to control Hg from transporting downstream in river systems, we demonstrated the effectiveness of a hydrologic weir at Wengman River of Wanshan Mercury Mining Area as a case study. Through a full year monitoring of mercury and its different species in water, we found the weir can retain 40.4% total Hg and 38.4% methylmercury due to longer residence time of water. Meanwhile, we confirmed waterflow was the dominant driver of particulate mercury, and much of mercury was released in high flow (e.g. storms) episodes. The total Hg and methylmercury balances and economic cost analysis proved weir construction is a cost effective method to control Hg pollution in contaminated areas.

Supplementary Information:

Weir building: a potential cost-effective method for reducing mercury leaching from abandoned mining tailings

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Supplementary Information:

YWM slagheap:

The slagheap of YWM is situated over 15 km in northeastern Wanshan County, in which approximately $3.1 \times 10^5 \text{ m}^3$ calcines were piled [1]. The tailing reservoir was designed to hold approximately $2 \times 10^6 \text{ m}^3$ calcines. Two dams were built in the tailing reservoir: the first dam was a gravity dam made of masonry and had a 690-m crest elevation, a 30-m length, a 1.2-m crest width, and a 15-m maximum height; the second dam was built 100 m downstream and had a 678-m crest elevation, a 27-m length, a 1-m dam crest width, and a 5-m maximum height. At present, the first dregs dam has been filled with silt, the slope of the heap is steep, the slope surface is not protected, and the erosion of the slope is serious. Rainwater caused calcines to pass the dam and travel downstream, which will accelerate the pollution of the Wengman River. This will pose direct threat to the safety of 2,800 people 5 km downstream.

Weir design:

Since the Wengman River is a small river, a weir trough was employed to determine the flow rate of water. According to the Code for Measurement of Discharge by Hydraulics Structures, Weirs and Flumes (SL537-2011) issued by the China Ministry of Water Resources, a V-type weir was selected. The weir is made of a stainless steel plate with a thickness of 1 cm.

Analysis:

THg and DHg were determined by BrCl oxidation and SnCl₂ reduction [2, 3], and a dual-stage Au amalgamation method and a Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS) were then used for detection [4]. Water samples were distilled, NaBEt₄ ethylated, and analyzed by cold vapor atomic fluorescence spectrometry (CVAFS) for MeHg analysis [5-7]. Specifically, a 45 mL aliquot sample was added to a Teflon distillation vessel on an Al heating pan and distilled at 170 °C for 3-4 h. The distillate then underwent aqueous phase ethylation by adding 0.2 mL 2

Supplementary Information:

M sodium acetate and 0.06 mL of 1% sodium tetraethylborate step by step, followed by purging with N₂ to absorb MeHg onto a Tenax trap [8]. MeHg was ultimately desorbed with heating on an isothermal GC column for peak separation and was analyzed by CVAFS (Brooks Rand Model III).

Anions and cations were determined by ICP-OES (Vista MPX, Varian) and IC (ICS-90, DIONEX). The DOC was measured using high-temperature catalytic oxidation [9].

Total suspended solids (TSS) were measured by filtering a 1.5 L water sample through a pre-weighed 0.45 mm cellulose filter. Then, the filters were oven-dried at 85 °C until the weight was constant [10]. The TSS weight was obtained by subtracting the weight (filter) from the total (filter + TSS).

Quality assurance and control of Hg analysis were assessed using blind duplicates, system blanks, method blanks, field blanks and matrix spikes. The relative standard deviation was found to be less than 10%, and the relative percentage difference of sample duplicates remained below 8%. The recoveries on spiked samples of TMeHg, DMeHg, THg and DHg ranged from 85% to 115%. The limit of determination for THg and DHg was 0.15 ng/L, as calculated by three times the standard deviation of the blank measurement. In addition, the limit of determination for TMeHg and DMeHg in water samples was 0.045 ng/L, which was three times the standard deviation of blanks.

Hydrological parameters

River discharge was calculated from stage monitoring data. A del triangle weir equipped with velocity measurement instrumentation was designed to measure the river flow. Precipitation data were obtained from the Chinese hydrologic station website in the nearest Tongren station. Temperature (T), pH, and total dissolved solids (TDS) were measured using a multi-parameter water analyzer (HACH HQ40d, USA).

Supplementary Information:

References:

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Supplementary Information:

Figures:

Fig. S1 The front view and top view of the weir.

Fig. S2 The correlation between flow and precipitation during one day.

Fig. S3 The daily water flow during sampling period.

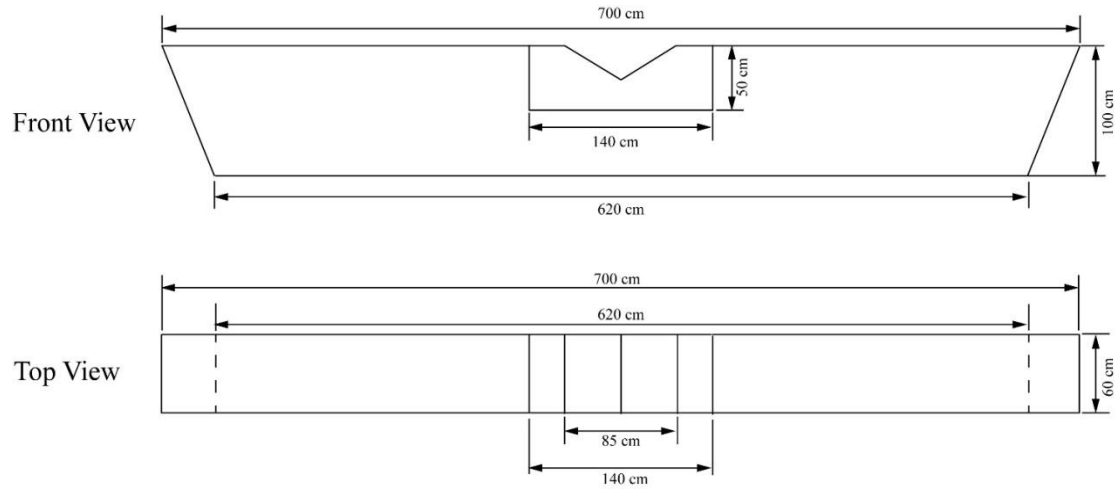


Fig. S1 The front view and top view of the weir.

Supplementary Information:

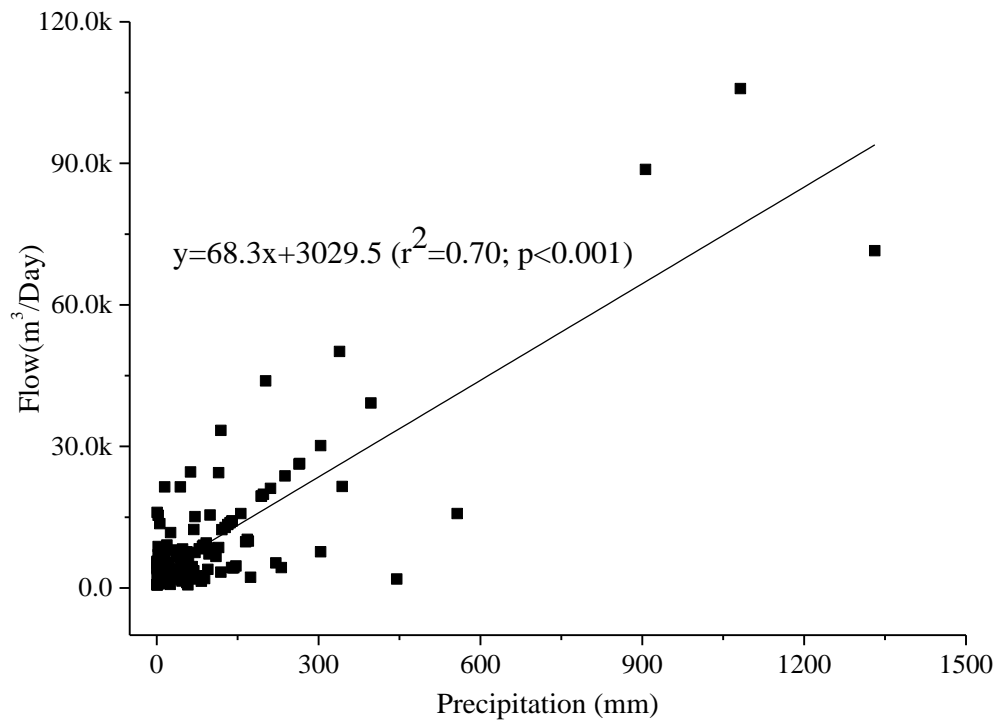


Fig. S2 The correlation between flow and precipitation during one day.

Supplementary Information:

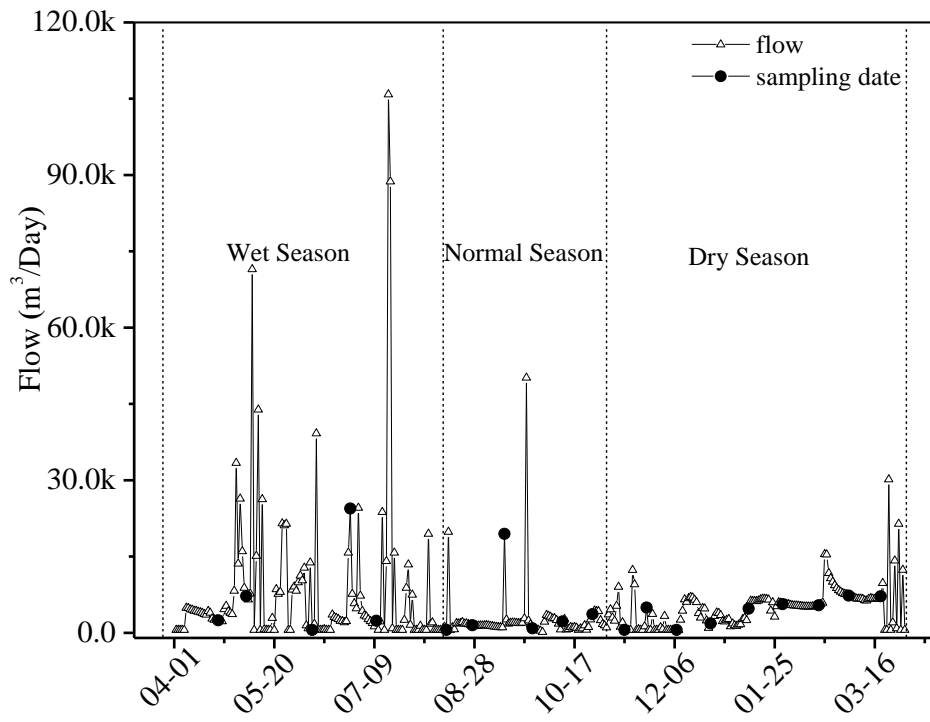


Fig. S3 The daily water flow during sampling period.

Supplementary Information:

Tables:

Table S1 Hg speciation at different sites in different seasons.

Table S2 Correlations between Hg speciation and additional parameters.

Table S3 Correlations between river discharge and Hg.

Table S4 Hg fraction during a rainstorm event.

Table S5 THg and DHg of calcines from Yanwuping slagheap.

Supplementary Information:

Table S1 Hg speciation at different sites in different seasons.

Sampling time	Sampling site	Mercury speciation (ng/L)					
		THg	DHg	PHg	TMeHg	DMeHg	PMeHg
wet season	Input site	296±285	59.9±37.3	236±253	3.22±2.84	1.25±0.670	1.98±2.36
	Internal site	200±257	43.0±29.0	157±233	2.67±2.22	0.910±0.590	1.76±1.75
	Output site	194±255	55.5±41.4	139±227	2.30±1.55	0.960±0.470	1.33±1.13
normal season	Input site	71.9±25.0	17.7±3.53	54.3±21.4	1.32±0.45	0.620±0.290	0.710±0.460
	Internal site	50.0±28.3	14.3±4.37	35.6±24.0	0.970±0.280	0.620±0.240	0.360±0.170
	Output site	38.8±20.9	12.8±3.41	26.0±17.5	0.760±0.440	0.450±0.130	0.310±0.340
dry season	Input site	21.9±5.42	12.0±2.50	9.90±6.42	0.370±0.170	0.220±0.080	0.150±0.160
	Internal site	19.2±4.87	12.3±3.48	19.7±4.64	0.350±0.080	0.240±0.070	0.110±0.060
	Output site	16.7±3.85	11.6±2.11	5.06±3.78	0.330±0.160	0.210±0.080	0.120±0.140

Supplementary Information:

Table S2 Correlations between Hg speciation and additional parameters.

	K ⁺	Ca ²⁺	Na ⁺	Mg ²⁺	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	DOC	TSS	THg	DHg	PHg	TMeHg	DMeHg	PMeHg
K ⁺	1.00															
Ca ²⁺	-0.550**	1.00														
Na ⁺	-0.100	0.430**	1.00													
Mg ²⁺	0.670**	-0.700**	-0.390**	1.00												
F ⁻	0.490**	-0.520**	-0.460**	0.600**	1.00											
Cl ⁻	0.850**	-0.510**	-0.100	0.510**	0.500**	1.00										
NO ₃ ⁻	-0.020	-0.040	-0.070	0.160	0.130	-0.250	1.00									
SO ₄ ²⁻	0.530**	-0.230	-0.170	0.350*	0.580**	0.640**	-0.010	1.00								
DOC	-0.560**	0.400**	0.140	-0.340*	-0.200	-0.510**	0.130	-0.300	1.00							
TSS	-0.610**	0.410**	0.230	-0.420**	-0.590**	-0.580**	0.220	-0.620**	0.300	1.00						
THg	-0.640**	0.310*	0.240	-0.430**	-0.530**	-0.640**	0.340*	-0.580**	0.350*	0.840**	1.00					
DHg	-0.770**	0.330*	0.250	-0.470**	-0.540**	-0.730**	0.220	-0.530**	0.480**	0.640**	0.850**	1.00				
PHg	-0.590**	0.300*	0.230	-0.400**	-0.520**	-0.600**	0.360*	-0.570**	0.320*	0.860**	0.990**	0.800**	1.00			
TMeHg	-0.710**	0.410**	0.410**	-0.550**	-0.590**	-0.660**	0.250	-0.560**	0.360*	0.830**	0.920**	0.820**	0.910**	1.00		
DMeHg	-0.710**	0.330*	0.390**	-0.560**	-0.630**	-0.670**	0.040	-0.600**	0.370*	0.670**	0.820**	0.860**	0.790**	0.880**	1.00	
PMeHg	-0.660**	0.420**	0.390**	-0.510**	-0.530**	-0.610**	0.310*	-0.500**	0.340*	0.840**	0.900**	0.750**	0.900**	0.980**	0.770**	1.00

*. Significant correlation at 0.05 level (two-tail)

** . Significant correlation at 0.01 level (two-tail)

Supplementary Information:

Table S3 Correlations between river discharge and Hg.

	River discharge	THg	MeHg
River discharge	1.00		
THg	0.680*	1.00	
MeHg	0.615*	0.935**	1.00

*. Significant correlation at 0.05 level (two-tail)

**.. Significant correlation at 0.01 level (two-tail)

Supplementary Information:

Table S4 Hg fraction during a rainstorm event

Time(min)	THg ($\mu\text{g/L}$)	DHg ($\mu\text{g/L}$)	PHg ($\mu\text{g/L}$)	PHg/ THg (%)
0	0.030	0.020	0.020	47.1
15	21.0	0.030	21.0	99.9
20	9.86	0.020	9.84	99.8
25	13.8	0.020	13.8	99.8
30	14.3	0.020	14.3	99.8
35	74.1	0.110	74.0	99.8
40	64.6	0.040	64.6	99.9
45	162	0.050	162	100
50	114	0.020	114	100
55	97.9	0.030	97.9	100
60	78.0	0.050	78.0	99.9
100	0.540	0.040	0.500	93.0

Supplementary Information:

Table S5 THg and DHg of calcines from Yanwuping slagheap.

Sample ID	THg (mg/kg)	DHg ($\mu\text{g/kg}$)
1#	41.0	7.60
2#	28.0	9.40
3#	13.0	2.20
4#	15.0	4.50
5#	15.0	3.60
6#	21.0	8.10
7#	30.0	12.0
8#	23.0	7.90
Mean	23.0	6.90