

The distribution and speciation of mercury in Wujiang river

H. Jiang^{1,2}, X. Feng¹, Q. Dai^{1,2}, F. Tao¹ and C. Liu¹

¹ *State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Science, Guiyang 550002, China*

² *Graduate School, Chinese Academy of Science, Beijing 100039, China*

Abstract. Concentrations of reactive, dissolved, particulate and total mercury in water samples were determined at 41 locations throughout the Wujiang River Basin, China. The sampling campaign was carried out 15–30 July 2002. During the collection of water samples for Hg analyses, other parameters were measured in situ (dissolved oxygen, pH, temperature and EC). The average concentration of the reactive mercury in surface water was 1.5 ng·L⁻¹. The concentration of total mercury ranged from 10.9 to 329.6 ng·L⁻¹, with a geometric mean of 44.4 ng·L⁻¹, and the dissolved mercury was from 1.0 to 49.2 ng·L⁻¹, with a geometric mean of 7.1 ng·L⁻¹. The proportion of reactive to total mercury was typically less than 5%, and the particulate to total mercury, with 90% of values higher than 50%. The pilot study indicated that Wujiang River is contaminated by mercury in a certain extent.

1. INTRODUCTION

Rivers are important sources of mercury (Hg) and methylmercury (MMHg) to estuaries and the coastal zone, contributing a significant fraction of the total Hg loading to these waters [1]. For example, a mass budget for the Chesapeake Bay suggests that about half the Hg input comes from fluvial sources, with the rest coming from atmospheric deposition [2]. Recent investigations have focused on the transformation processes of Hg in rivers [3–8], the biogeochemical cycling of mercury in rivers is still however under studied especially in China. This is partly due to the difficulty in obtaining reliable data at picomolar concentration levels in nature waters, and to the diversity and complicated distribution of the stable chemical species of Hg, including ionic, volatile and poorly soluble compounds. Here, we report the result of a pilot study on Hg concentrations and speciation in surface water from the Wujiang River Basin to improve our understanding of mercury biogeochemical cycling in fresh water system. To our knowledge, it is the first comprehensive study on mercury distribution and speciation in river system in China.

2. EXPERIMENTAL SECTION

2.1 Sampling Site

Wujiang River flowing in a Karst environment in Guizhou Province and having two main tributaries at the upper reach (the Sancha River and the Liucong River) is the largest tributary in the upstream of Yangtze River. It covers a drainage area of approximately 87,920 km², with an average stream flow of over 650 m³/s and an annual runoff of 5400000 hm³. The drainage area is located in a typical subtropical moist climate zone, where atmospheric temperature, precipitation and humidity are relatively high, and the chemical weathering is relatively strong. Its drainage lies on a natural mercuriferous belt, which is

also a part of the huge low temperature epithermal mineralization zone of SW China. The bedrocks of the drainage area of Wujiang River are strongly enriched in trace elements associated with epithermal precious-metal deposits (e.g., Au, Ag, Hg, Sb, As and U). Thus, Wujiang drainage basin would be an important mercury source to the Three-Gorge Reservoir region once the dam is constructed. It is, therefore, obviously that the study of the behavior and the fate of mercury in Wujiang River is essential in understanding the relationship between the chemical weathering of carbonate rock and the characteristic of the mercury biogeochemistry, and in predicting future impact on methylmercury contamination in the Three-Gorge Dam.

2.2 Methods and materials

In July 2002, water samplers were collected along Wujiang River Basin. Clean polyethylene gloves were worn to collect water samples using a pre-cleaned Teflon bottle. We collected water samples manually while wading slowly up stream, or collected samples by hand from a wood boat moving gently against the current during sampling, by submerging Teflon (FEP) approximately 20 cm beneath the water surface to prevent contamination of the water sample. Both filtered and unfiltered water samples were collected. Filtered samples were prepared using 0.45- μm nylon membrane filters. Water samples for Hg analysis were collected in pre-cleaned, borosilicate glass bottles. At the field site, the bottles were rinsed three times with the sampled water prior to filling, then filled, and preserved with sub-boiling distilled HCl to yield 0.5% acid solutions, and tightly sealed and double-bagged and stored in a wood box. After being transported back to the laboratory, the samples were stored at +4°C in the dark until the analyses were performed. The filters were sealed in PE bags and stored deeply frozen. Analysis was performed on the wet filters. Each batch of filters and bottles were analyzed before uses to check the blank.

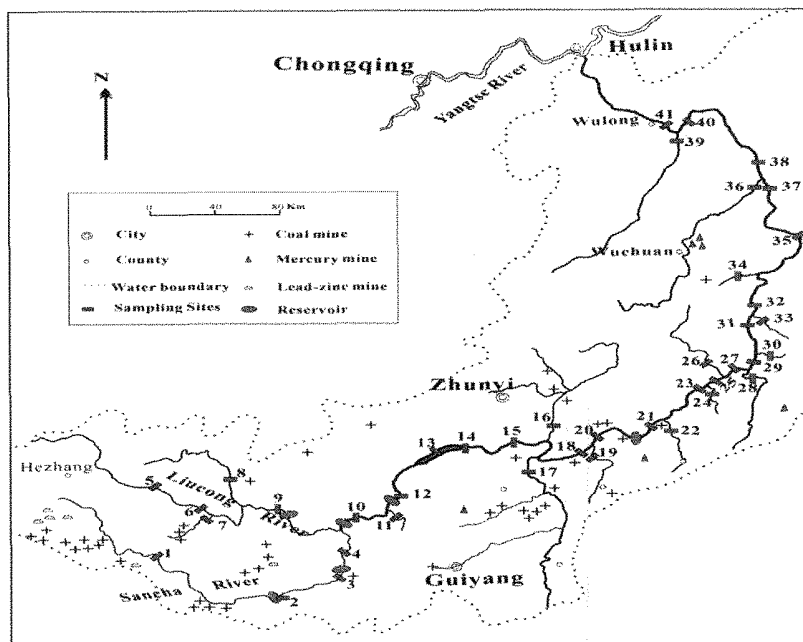


Figure 1. The locations of Hg mines, coal mines and Lead-Zinc mines as well as sampling locations in Wujiang river basin.

Analyses of Hg in water samples were completed using gold trap pre-concentration and CVAFS detection method (Tekran 2500) according to the US Environmental Protection Agency (EPA) Method

1631 [9]. The successive steps to determine total particulate Hg were: (1) digesting the filters in 4 ml HNO_3/HCl (3:1) in microwave oven in Teflon digestion vessels; (2) diluting the sample to 100 ml; (3) analysis of a fraction of the sample by CVAFS as described above. Water characteristics such as pH, temperature, conductivity, dissolved oxygen, and alkalinity were measured on-site.

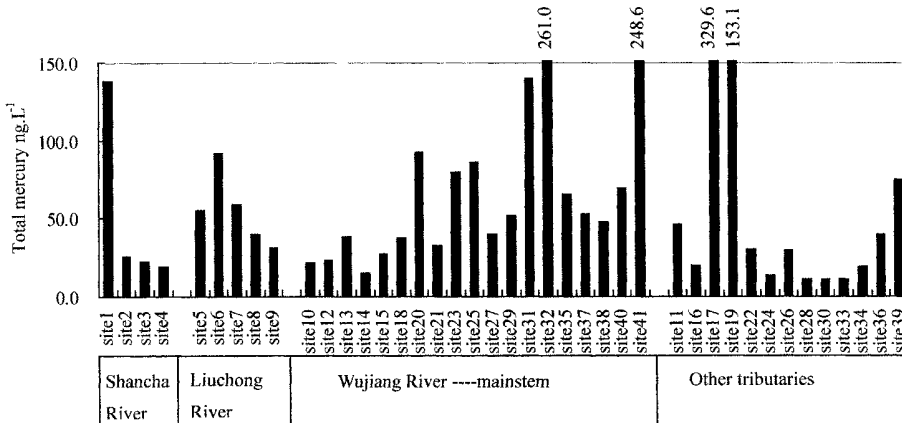


Figure 2. Concentrations of total mercury in surface water

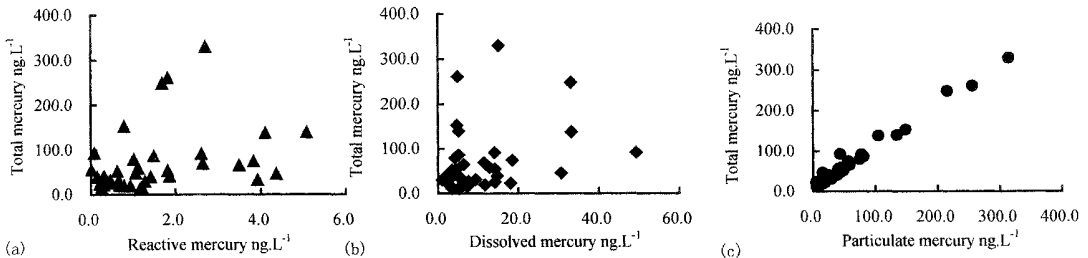


Figure 3. Plot of total Hg vs. Hg_R (a), Hg_{TD} (b) and Hg_P (c) in surface water

3. RESULTS AND DISCUSSION

Total Hg (Hg_T) concentrations ranged from 10.9 to 329.6 ng. L^{-1} , with a geometric mean of 44.4 ng. L^{-1} (Fig.2). The distribution of Hg_T in the Sancha River, one of the headstream of the Wujiang River, indicated the existence of the reservoirs behaves as an artificial sink of Hg, where sedimentation occurs, reducing both the turbidity and the Hg concentration of water. Because the samples were obtained immediately following the rain season, the Wujiang River especially in the middle and down stream had a strong current. The total Hg shows a dramatic increase in concentration under high flow conditions, especially in site 19, 31, and 32, and the high total Hg concentrations are probably resulted from re-suspension of the particulate. The water samples, which were collected in the vicinity of urban centers (site 17,41), or of the coal mines, lead-zinc mines (site 1,17), had elevated total mercury concentrations. It was expected that the highest concentrations might be found at Hongdu Creek, site 36, because that site is the downstream of the Wuchuan mercury mines. The presence of the mercury mines does not lead, however, to an enrichment in Hg in either the filtered or the particulate fraction, which may also be attributed to the upstream reservoir that probably traps most of the mercury associated with the particles.

Reactive mercury (Hg_R) concentrations, mostly inorganic $Hg(II)$, ranged from the detection limit to $5.1 \text{ ng} \cdot \text{L}^{-1}$, with an average of $1.5 \text{ ng} \cdot \text{L}^{-1}$ (Fig.3a). The Hg_R/Hg_T ratios varied from <1% to 12%, and was typically less than 5%. The dissolved mercury (Hg_{TD}) was from 1.0 to $49.2 \text{ ng} \cdot \text{L}^{-1}$, with a geometric mean of $7.1 \text{ ng} \cdot \text{L}^{-1}$, and represented 1.9-77.6% of Hg_T in surface water (Fig.3b). The particulate Hg (Hg_P) varied from 5.2 to $314.4 \text{ ng} \cdot \text{L}^{-1}$ (Fig.3c), and the proportion of which to total mercury was higher than 50% in 90% water samples. It showed that total Hg burdens are governed by the quantity of the suspended matters in the water column.

Sampling for reactive, dissolved, particulate and total mercury within the Wujiang River watershed have shown, at least for the high flow period, that concentrations and loads tend to be much higher than those reported about other river waters, such as the St. Lawrence river [7] and the Tapajos River Basin [8]. The findings of this study indicate the need to examine and identify the sources and the bioavailability of mercury in the aquatic system, and the potential methods for remediation or environmental cleanup.

Acknowledgements

This work was financially supported by Chinese Academy of Sciences through "Hundred Talent Plan" and CAS innovation project (KZCX2-105), and by Chinese Natural Science Foundation (40173037).

References

- [1] Cossa, D., Coquery, M., Gobeil, C. and Martin, J. M., Mercury fluxes at the ocean margins. In Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances. (Baeyens W. et.al., Kluwer, Netherlands, 1996) pp.229-247.
- [2] Mason, R. P., Lawson, N. M. and Sullivan, K. A., *Atmos. Environ.* **31**(1997a) 3531-3540.
- [3] Carroll, R. W. H., Warwick, J.J., Heim, K.J., Bonzongo, J. C., Miller, J. R., Lyons, W. B., *Eco. Model.* **125** (2000) 255-278.
- [4] Domagalski, J., *Appl. Geochem.* **16** (2001)1677-1691.
- [5] Domagalski, J., *J. Geochem. Explor.* **64**(1998)277-291.
- [6] Hurley, J. P., Benoit, J. M., Babiarz, C. L., Shafer, M. M., Andren, A. W., Sullivan, J. R., Hammond, R. and Webb, D. A., *Environ. Sci. Technol.* **29**(1995)1867-1875.
- [7] Qu  merais, B., Cossa, D., Rondeau, B., Pham, T. T. and Fortin, B., *Sci. Total Environ.* **213** (1998) 193-201.
- [8] Roulet, M., Lucotte, M., Canuel, R., Rheault, I., Tran, S., De Freitas Gog, Y. G., Farella, N., Souza do Vale, R., Sousa Passos, C. J., De Jesus da Silva, E., Mergler, D., Amorim, M., *Sci. Total Environ.* **213** (1998)203-211.
- [9] US EPA, Method 1631, Revision B: Mercury in water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. United States Environmental Protection Agency, Office of Water 4303, EPA- 821-R-99-005, 1999.