Sources and Pollution Assessment of Mercury in the Li River System, Guangxi, China

Jianping QIAN *[1], Li ZHANG [2], Yunfei NIU [3], Chao CAO[1],Guilian LIANG [2], Wenying JIANG [2], Ming XU [1], Sha JIANG [1]

[1]*College of Earth Sciences, Guilin University of Technology, 541004, Guilin, China*
[2]*College of Environmental Science and Engineering, Guilin University of Technology, 541004, Guilin, China*
[3]*Wuhu Guozhen Environmental Protection Sci. & Tech. Co., Ltd, 241000,Wuhu, China*
Email: jpqian@163.com

Abstract: A series of samples included 112 water samples, 40 sediment samples, 40 aquatic plants and 40 near-shore soil samples were collected from the 40 sampling sites in the mainstream and tributaries of the Li River, Guangxi Provence of PR China. The mean value of the total mercury (THg) content in the mainstream of the Li River was found to be 0.12μg/L in water, 0.20μg/g in bottom mud, 0.032μg/g in float grass. The THg mean content in main tributaries of the Li River was 0.15-0.23μg/L in water, 0.38-1.7μg/g in bottom mud, 0.028-0.044μg/g in float grass, which was higher than that in the mainstream. The THg content in river water was correlative with that in bottom mud and float grass and increased from the upstream to the downstream whether in the mainstream or in main tributaries. The THg in the river water in the rainy season was much higher than that in the dry season. These results indicated that the largest sink of Hg contamination of Guilin City was the mainstream of the Li River. According to surface water environment quality standards of China (GB3838-2002), the water Hg level of the Li River satisfied grade IV quality ($Hg \leq 1\mu g/L$)

Keywords: mercury (Hg); bottom mud; aquatic plants; Li River

1 Introduction

Many Chinese cities have been built on the banks of a river. Compared with rivers in general, the impact of human activities on the hydrological features, physical composition and ecological environment of urban streams is more serious. Urban rivers are the receptors of urban pollutants. With the accelerated development of urbanization, the mercury pollution in the urban environment is getting more and more serious.

The Li River is a famous tourist destination in China and the most important water source of the city of Guilin. In the present study, mercury pollution of the Li River system was comprehensively investigated, and the pollution status and distribution of Hg pollution were also analyzed. The pollution assessment of mercury in the Li River was helpful in making reasonable countermeasures for the protection of the ecological environment in the Li River system.

2 Methods

The Li River originates from Maoer Mountain which is located about 110 km north of Guilin. The mainstream and three tributaries of the Li River flow through Guilin. The tributaries are, from north to south, the Taohua River, Xiaodong River and Nanxi River.Ling-

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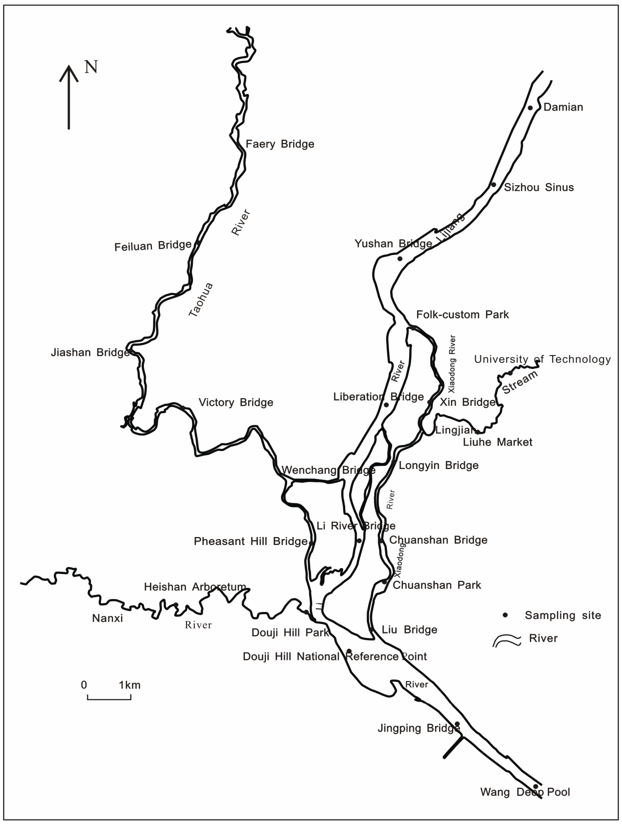

Figure 1 Sampling sites in Li River system in Guilin city zone

jian Stream is a sub tributary originating from the upstream area of the Xiaodong River. There are 8 sampling sites in the upstream of the Li River, 7 sites in the urban district, and 16 sites in tributaries (6 in the Taohua, 6 in the Xiaodong, 2 in the Nanxi and 2 in the Lingjian Stream) (Figure 1).

The samples were collected during the rainy and dry seasons in two hydrologic years (from March to the following February), and included river water, bottom mud, riverbank soil, and float grass. Bottom mud was not collected during the rainy season. The float grass plants were pulled up by their roots and the silt was removed. The plants were then soaked for 10min in deionized water, divided into root, stem and leaf and dried at a temperature of 38-42℃ for 3-4 days. The dried plants were ground and passed through 180μm nylon screen, and then stored in an exsiccator. The bottom mud and soil samples were air-dried, ground and passed through a 96μm nylon screen, and then stored in an exsiccator. The river water was collected avoiding drainage outlets, and the electrical conductivity, temperature, and pH value were measured on the spot. Then the samples were taken to the laboratory using a polytetrafluoroethylene container, nitric acid was added, and they were stored at low temperature.

Soil, bottom mud and float grass samples were digested by a microwave system (MDS-2003F) for total mercury (THg). Each 0.3g soil and bottom mud sample was put into the sample dissolution tin and 4mL nitric acid was added. After 30min soaking, 2mL sulfuric acid was added slowly. After 10min soaking, the sample was digested. Each 0.5g plant sample was put into the sample dissolution tin and 5mL nitric acid was added. After 30min soaking, 2mL peroxide was added slowly. After 10min soaking, each sample was digested using the microwave system.

The total Hg from the river water samples was separated and enriched with sulfhydryl cotton. The sulfhydryl cotton was washed with a little deionized water and moistened with 4mL hydrochloric acid with a pH value of 3-4. Then the 2L river water samples flowed through the sulfhydryl cotton with a 8-10mL/min flow speed. The Hg in sulfhydryl cotton was washed out using a 6mL saturated NaCl-HCl solution, then was collected in a 10mL colorimetric tube and 0.5mL bromide was added. Before testing, oxammonium hydrochloride (50g/L) was added to reduce superfluous bromide.

The Hg concentrations in different fractions of bottom mud were investigated by the sequential extraction method according to the description of Hou et al. (2005). The methyl mercury (MeHg) in bottom mud was determined by GC-CVAFS after Aqueous Phase Ethylation (He et al. 2004).

The total Hg in samples was examined by FI-HG-CAAS (FI-AAS-700, PerkinElmer) after digestion. The limit of detection was 0.039μg/L. National standard materials (GBW07405 for soil, GBW10015 for plants) and the standard material IAEA-40 for bottom mud were used for quality control. The average recoveries of Hg in soil was 86%, in plants was 93%. The average recovery of MeHg in bottom mud was 80%.

3 Results and Discussion

The mean value of the total mercury content in the mainstream of the Li River was 0.12μg/L in the river water, 0.20μg/g in the bottom mud and 0.032μg/g in the float grass (Table 1).

Table 1 Physicochemical properties and THg in different kinds of samples in the mainstream of the Li River (October 2006)

Sampling points	Electrical conductivity (μs/cm)	pH	River water (μg/L)	Bottom mud (μg/g)	Near-shore soil (μg/g)	Float grass (μg/g)
Maoer Mountain (upriver area)	7.67	7.50	0.051	0.083	0.073	--
Liudong River	104	7.50	0.058	0.10	0.078	--
Darong River	105	7.32	0.075	0.12	0.089	--
Three Streets Town	112	7.53	0.10	0.12	0.084	--
Damian National Reference Point	155	7.30	0.091	0.10	0.099	0.023
Sizhou Bay	166	7.14	0.086	0.14	0.096	0.021
Yushan Bridge	177	7.10	0.099	0.23	0.14	0.030
Liberation Bridge	187	6.96	0.11	0.26	0.21	0.034
Lijiang River Bridge	179	8.39	0.20	0.29	0.30	0.035
Douji Hill National Reference Point	201	7.83	0.23	0.31	0.32	0.036
Jingping Bridge (downriver area)	196	8.42	0.27	0.46	0.40	0.044
Mean value			0.12	0.20	0.17	0.032

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The mean value of the total mercury content in the main tributaries (Taohua River, Xiaodong River, Nanxi River and Lingjian Stream) was 0.15-0.23μg/L in the river water, 0.38-1.7μg/g in the bottom mud and 0.028-0.044μg/g in the float grass, which were all higher than that in mainstream. In the area encompassing the Taohua (Taohua on Figure 1), Xiaodong, Nanxi rivers and the Lingjian Stream, the water flow of the tributaries is decreasing and thus the dilution effect of the upper waters is waning. This developed area is closer to the urban core, making the contamination of Hg more serious (Table 2).

The mean value of THg content, whether in mainstream or tributaries, all followed the rule: bottom > float grass > water. The THg in the bottom mud was higher than that in the riverbank soil, indicating that the Hg in this bottom mud does not merely come from riverbank soil.

The THg of river water was significantly correlated with that of bottom mud and float grass whether in the mainstream or tributaries(Table 3), indicating that the Hg in water was the main source of Hg pollution of bottom mud, and the Hg in bottom mud could transfer to hydrophytes by the riverine ecosystem.

From upriver to downriver areas, the total mercury contents of water in mainstream and tributaries have all increased. The THg in the downriver water was 1.5-5 times higher than that in the headstream water (Table 1, Table 2). The reference index of heavy metal pollution -- electrical conductivity also increased (Su et al. 2003). The river water flows from the source region through Caledonia granitoid, Proterozoic and Eopaleozoic metamorphic rock, Neopaleozoic clastic rock and Neopaleozoic carbonatite regions with increasing pH value. However the THg in the upriver area was higher than that in the downriver area in Lingjian Stream because the Lingjian is a tributary of the Xiaodong River, with a short and narrow flow path and slow flow speed, and the upriver area of Lingjian Stream is located in villages within the city, where it is affected by riverbank trash.

Table 2 Physicochemical properties and total mercury content in different kinds of samples in the tributaries of the Li River (October 2006)

Sampling points		Electrical conductivity（μs/cm）	pH	River water（μg/L）	Bottom mud（μg/g）	Near-shore soil（μg/g）	Float grass（μg/g）
Taohua River	Faery Bridge (upriver area)	149	7.15	0.14	0.098	0.052	0.031
	Feiluan Bridge	165	7.16	0.14	0.24	0.29	0.042
	Jiashan Bridge	196	7.26	0.16	0.40	0.38	0.046
	Victory Bridge	190	7.42	0.15	0.28	0.37	0.042
	Wenchang Bridge	182	7.84	0.25	0.52	0.36	0.047
	Pheasant Hill Bridge (downriver area)	179	7.82	0.26	0.61	0.39	0.057
	Mean value			0.18	0.36	0.31	0.044
Xiaodong River	Folk-custom Park（upriver area）	237	6.87	0.11	0.10	0.087	0.019
	Xin Bridge	294	6.86	0.14	0.38	0.36	0.022
	Longyin Bridge	536	7.58	0.14	0.43	0.38	0.021
	Chuanshan Bridge	464	7.59	0.16	0.62	0.51	0.030
	Chuanshan Park	442	7.34	0.15	0.62	0.39	0.036
	Lius Bridge（downriver area）	456	7.37	0.22	0.80	0.44	0.039
	Mean value			0.15	0.49	0.36	0.028
Nanxi River	Heishan Arboretum (upriver area)	213	7.47	0.17	1.1	0.26	---
	Nanxishan Park (downriver area)	351	7.98	0.19	1.3	0.43	---
	Mean value			0.18	1.2	0.34	---
Lingjian Stream	University of Technology (upriver area)	744	7.37	0.24	2.2	0.24	---
	Liuhe Market (downriver area)	586	6.80	0.22	1.1	0.26	---
	Mean value			0.23	1.7	0.25	---

The total mercury content in the river water in the rainy season (May and June) was much higher than that in the dry season (September to November) (0.12-0.28μg/L in the rainy season, 0.091-0.28μg/L in the dry season) (Table 4). The result was agreed by Donkor et al. (2006) and Daniel et al. (2007). The high THg in water in the rainy season could be ascribed to the serious non-point source pollution.

The Li River is a typical rain-oriented river. Due to the monsoon climate, flood season of the Li River often

Table 3 Correlation analysis of Hg content between different samples of the mainstream and main tributaries of the Li River

Sampling sites	Correlation coefficient	River water	Bottom mud	Float grass	Critical value
Mainstream	River water	1	0.889	0.883	
	Bottom mud	0.889	1	0.981	$r_{5,\ 0.05}$= 0.754
	Float grass	0.883	0.981	1	
Taohua River	(River water	1	0.827	0.785	
	Bottom mud	0.827	1	0.926	$r_{4,\ 0.05}$=0.811
	Float grass	0.785	0.926	1	
Xiaodong River	River water	1	0.917	0.852	
	Bottom mud	0.917	1	0.905	$r_{4,\ 0.05}$=0.811
	Float grass	0.852	0.905	1	

Table 4 Comparison of THg between dry season and rainy season in various water bodies of the Li River system

Rivers	Number	Sampling points	2006		2007	
			Rainy season （μg/L）	Dry season （μg/L）	Rainy season （μg/L）	Dry season（μg/L）
Mainstream of Li River	1	Damian National Reference Point	0.10	--	0.12	0.091
	2	Yushan Bridge	0.11	0.099	0.12	0.10
	3	Liberation Bridge	0.13	0.11	0.13	0.11
	4	Li River Bridge	0.20	0.20	0.22	0.19
	5	Douji Hill National Reference Point	--	0.23	0.24	0.26
	6	Jingping Bridge	0.28	0.27	0.28	0.28
Taohua River	7	Faery Bridge	0.15	0.14	0.14	0.14
	8	Feiluan Bridge	0.15	0.14	0.16	0.14
	9	Jiashan Bridge	0.16	0.15	0.16	0.15
	10	Victory Bridge	0.20	0.16	0.20	0.16
	11	Wenchang Bridge	0.26	0.25	0.26	--
	12	Pheasant Hill Bridge	--	0.26	--	0.26
Xiaodong River	13	Xin Bridge	0.14	0.14	0.15	0.13
	14	Longyin Bridge	0.16	0.14	0.17	0.13
	15	Chuanshan Bridge	0.18	--	0.21	0.14
	16	Chuanshan Park	0.17	0.15	--	0.14
Nanxi River	17	Heishan Arboretum	0.19	0.17	0.20	0.17
	18	Nanxishan Park	0.20	0.19	0.20	0.18
Lingjian Stream	19	University of Technology	0.26	0.24	0.24	0.21
	20	Liuhe Market	0.23	0.22	0.22	0.20

occurs from March to August. The rainfall in this period accounted for 76% of the annual rainfall, while the runoff accounted for 81.9% of the annual runoff. The Hg in rain might be the original source of Hg in the Li River.

The Hg content of rain in Guilin from April 2008 to March 2009, was 0.014-0.054 $\mu g \cdot L^{-1}$, with an annual mean of 0.028$\mu g \cdot L^{-1}$.

The drops of rainwater converged into little rivulets and streams and finally formed the headstream of the Li River with high water quality and the Hg content of and

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0.0514 μg·L^{-1}, caused by washing the sloping granite mountain massif of Maoer Mountain, scouring the trench infiltration. The Hg content was up to 0.086 μg·L^{-1} before entering the city zone, as a result of the water-rock interaction in the upriver area and the input of agricultural pollutants.

It was self-evident that industrial waste and domestic waste were the main sources of Hg pollution in the Li River. With the input of pollutant from tributaries and riverbanks, the Hg content of the Li River reached 0.27μg·L^{-1} at Jingping Bridge (Table 1).

The source region and upriver area of the Li River are in steep terrain. In the flood period, huge amounts of surface runoff were formed instantaneously, the alimentation area enlarged rapidly, non-point source pollutants with different sources and a wide range came together, and thus the Hg contamination degree of Li River increased, showing significant fluctuations.

It could be concluded that the total mercury contents of water, bottom mud and float grass in the mainstream and tributaries all increased from upriver to downriver areas and the reference index of heavy metal pollution - electrical conductivity enhanced correspondingly. The mean of total mercury content in bottom mud was higher than that in riverbank soil. The distribution of Hg fractions in the bottom mud of the Li River system was consistent with the soil Hg fractions on the bank. The THg in the river water during the rainy season was much higher than that in the dry season. These results indicated that the largest sink of Hg contamination of Guilin City was the mainstream of the Li River.

According to surface water environment quality standards of China (GB3838-2002), the water Hg level of the Li River satisfied grade IV quality (Hg ≤ 1μg/L). Compared with other typical rivers (Table 5), the THg of the Li River in the city was higher than average.

To assess heavy metal pollution in water bodies and sediments, not only the human factors but also the natural factors that may cause change of background level (constant) should be considered. The geoaccumulation method compensates for the shortcomings of other methods. The geoaccumulation index is calculated using the following equation:

$$I_{geo} = log_2 \left[C_n / \left(1.5 \times BE_n \right) \right]$$

where C_n is the content of Hg in samples, BE_n is the background level of Hg and the modified coefficient is 1.5 in the present work. The index of geoaccumulation was divided into 7 ranks. Ranks of 0-6 expressed the degree of contamination from non-pollution to most severe pollution. The content of element in rank 6 might be hundreds of times higher than background level (Teng et al. 2002).

Analysis and assessment results of samples collected from the headstream of the Li River indicated that the environment quality of the headstream was not polluted according to surface water environment quality standards of China (GB3838-2002). Therefore, the THg in headstream samples could be regarded as background values. The background value was 0.083μg/g in bottom mud. The status of mercury contamination in the Li River assessed by the geoaccumulation method showed that there were different degrees of pollution both in the mainstream and the tributaries in the urban section of the Li River. The bottom mud in the suburban section of the mainstream was assigned the rank of non-pollution, the urban section of the mainstream, Taohua River and Xiaodong River were ranked light pollution, while the Nanxi River and Lingjian Stream were ranked moderately high pollution.

Table 5 Comparison of the Thg content of the Li River and other rivers at home and abroad

Period	River	Total Hg content /(μg·L^{-1})	References
2005	Songhua River	0. 096	HW Li et al. (2006)
2005	Heihong River	0. 043	HW Li et al. (2006)
2005	Wusuli River	0. 068	HW Li et al. (2006)
2005	Douro River in Portugal	0. 0006~0. 0065	Ramalhosa E et al. 2005
2005	Cecina river basin, Italy	0. 035	Scerbo R et al. 2005
1990s	Tapajos River Basin, Brazilian Amazon	0. 0007~0. 0159	Roulet M et al. 1998
2007	Hengyang section of Hsiang River	0.041~0. 071	CX Li et al. 2007
2006	Li River	0.051~0.27	This study

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