CHEMICAL ENGINEERING TRANSACTIONS

VOL. 59, 2017

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Zhuo Yang, Junjie Ba, Jing Pan

ISBN 978-88-95608- 49-5; **ISSN** 2283-9216

DOI: 10.3303/CET1759148

Environmental Chemistry of Toxic Heavy Metals Hg-As in the Jialing River

Xianmin Wang[a*], Feng Yang[b], Xiaoli Chen[a], Shaoxia Yang[a]

[a]Guangdong Ocean University, Zhanjiang 524088, China;
[b]Zhanjiang oceanic and fishery environmental monitoring station, Zhanjiang 524039, China
xianmin810@163.com

Targeted at the natural water body in the Jialing River, this paper takes the environmental chemistry perspective to compare the heavy metal (Hg, As) distribution characteristics in the surface water, suspended particulate matter and fish, the typical living being, of the water body in the Jialing River. After measuring the rough contents of the two heavy metals in the natural water body of the Jialing River, it is concluded that the degree of Hg pollution is lightly polluted and that of As pollution is clean. The author also analyzes the main factors influencing the difference of metal content in each phase, pointing out that the content of dissolved Hg in the aqueous phase is significantly higher in the downstream than the upstream. Furthermore, the research reveals that the fish in the river bears insignificant latent health risks, and As poses more risk than Hg in fish eating.

1. Introduction

Among the many water pollutants, heavy metals stand out as an important category of potentially harmful pollutants (Burrows and Whitton, 1983; Kozhenkova et al., 2000; Ismail et al., 2016). Featuring latent, long-lasting and irreversible effect, the heavy metals cannot be permanently removed (Bhosale and Sahu, 1991; Bhosale and Sahu, 2015; Shirkhanloo et al., 2015). Owing to these features, the migration, transformation and the final chemical attribution of heavy metals in natural water bodies have long attracted the attention of environmental scientists. These issues call for long-term and systematic research. Much efforts are yet to be paid to examine the content, level, and vertical distribution of toxic heavy metals in natural water bodies, as well as to disclose their occurrence state and the law of migration and transformation. It is of great theoretical value and practical significance to carry out the above studies for understanding the status quo and distribution pattern of heavy metals in water bodies and for tracing the possible heavy metal pollution (Krishna et al., 2009; Bai et al., 2012; Gümgüm et al., 1994; Zhao et al., 2016; Lozano et al., 2016;).

This paper measures the rough contents and distribution characteristics of the heavy metals (Hg, As) in the surface water, suspended particulate matter and fish of the water body in the Jialing River, conducts water quality evaluation and risk assessment, and explores the difference in morphological distribution of heavy metals (Hg, As) and the correlation effect between heavy metals and basic water quality parameters, aiming to disclose the environmental chemistry characteristics of heavy metal pollution in the food chain system of the Jialing River water-suspended matter-fish.

2. Experimental content

2.1 Selection of sampling points and collection of samples

16 places were taken from the upstream to the downstream of the Jialing River as the sampling points, including Qukou, Qujiang River, Second Fujiang River Bridge, Jingshui Temple, Diaoyu Fortress, Chengjiang River, a tributary to Chengjiang River, Beibei Water Plant, Mingjia Stream, Longfeng Stream, Chaoyangqiao, Jingkou, Ciqikou, Zhongdukou, Hualongqiao, and Chaotianmen, and denoted as S1~S16, respectively. Besides, fixed-volume surface water samples were collected from the left, middle and right of each sampling point. In total, six types of fish were caught along the Jialing River, namely Pseudobagrus emarginatus,

Please cite this article as: Xianmin Wang, Feng Yang, Xiaoli Chen, Shaoxia Yang, 2017, Environmental chemistry of toxic heavy metals hg-as in the jialing river, Chemical Engineering Transactions, 59, 883-888 DOI:10.3303/CET1759148

Hemibarbus maculatus Bleeker, Mystus macropterus Bleeker, Carassius auratus, Acrossocheilus monticola, and carp, and denoted as F1~F6.

2.2 Pretreatment of samples

2.2.1 Water samples and suspended matter samples

After being transported to the lab, the water samples were filtered through a 0.4 μm microfiltration membrane and acidified to pH<2 with a GR HNO_3 for preservation. The filtered suspension was dried at 103 °C, and the suspension concentration was measured.

2.2.2 Analysis and digestion of heavy metals

The unfiltered water samples were digested by microwave for the measurement of the total state metal concentration. Then, the filtered water sampled were monitored to get the dissolved state metal concentration. The total heavy metal content was obtained by deducting the dissolved state metal concentration from the total state metal concentration.

2.2.3 Digestion of fish samples

Each of fish samples was processed in the following steps: wash the fish clean, measure the body length and weight, and cut it open to extract the flesh and liver; weight a proper amount (0.1~0.3g) of tissues from the fish sample, put it into a microwave digestion tube, add 5mL HNO_3, and place the tube in a microwave oven for digestion. The digestion was carried out according to the preset heating digestion procedure (Table 1). After the digestion was completed, remove the acid, relocate the tissues into a 25mL colorimetric tube, and dilute it with distilled water to a certain volume for further treatment.

Table 1: Microwave digestion procedure

	Power/W	Energy/%	Up time/min	Temperature/C	Maintain time/min
1	600	100	05:00	120	05:00
2	600	100	10:00	170	15:00

2.3 Instruments and reagents

The instruments include MARSxPress microwave digestion system, AFS-230E atomic fluorescence spectrometer, PHA-3D precision sound level meter, AL104 electronic balance, DDS-307 conductivity meter, HACH portable DO, and oxidation-reduction potentiometer IL500TOC-TN.

2.4 Sample analysis

The heavy metals Hg and As are measured by double-channel hydride generation atomic fluorescence spectrometry (Alonso et al., 2004; Sharifi et al., 2016; Prasanna et al., 2012).

3. Experimental results

3.1 Spatial distribution characteristics of dissolved heavy metals in the Jialing River

The average concentrations of dissolved As and Hg in the water samples are 1.55 and 0.64μg / L, respectively. The spatial pattern of heavy metals in the water of the Jialing River is analyzed by the average concentration of dissolved heavy metals in the water samples collected at each sampling point. It can be seen from figure 1 as follows.

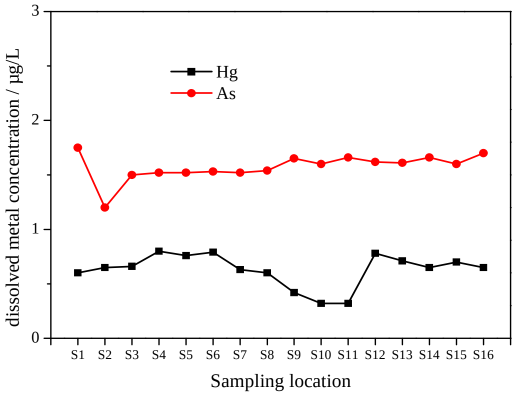

Figure 1: Spatial distribution map of dissolved heavy metal concentrations

As shown in Figure 1, there is no obvious locational variation in the content of dissolved As from the upstream to the downstream. In contrast, the content of dissolved Hg in the aqueous phase is significantly higher in the downstream than the upstream, especially downstream the sampling point of Ciqikou. The growing trend is probably caused by the gradual increase of industrial and domestic wastewater after the river flows into the city proper of Chongqing.

3.2 Distribution of heavy metals in solid phase and liquid phase

3.2.1 Dominant form of heavy metals in the water of the Jialing River

Figure 2 illustrates the distribution of heavy metals As and Hg in the dissolved state and granular state.

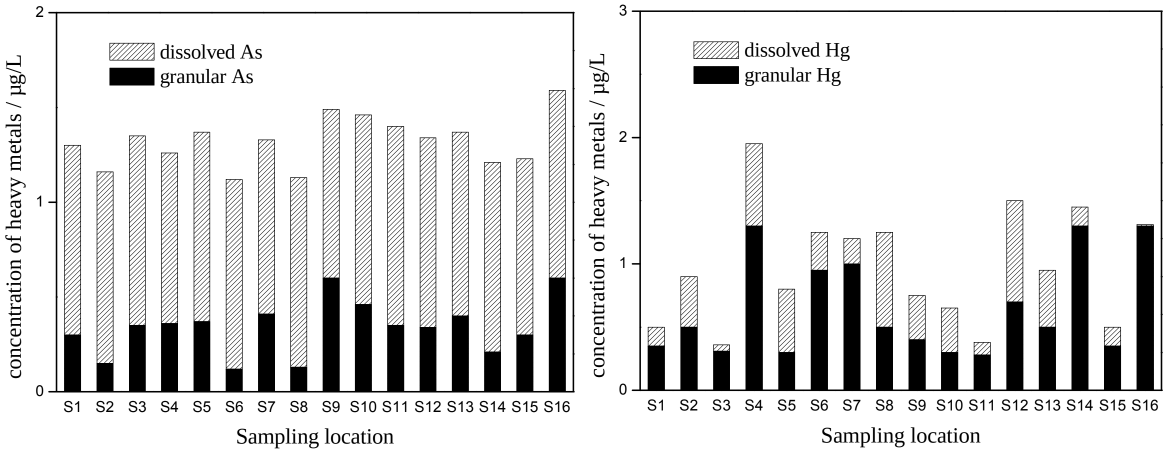

Figure 2: State distribution of heavy metals

It can be seen from Figure 2 that As in the water of the Jialing River mainly exists in the dissolved state, while Hg in granular state. The state distribution is closely related to the variation in suspended matter concentration.

3.2.2 Effect of suspended matter concentration on heavy metal distribution

The heavy metal elements entering the river are either directly dissolved in water or adsorbed by suspended solids in the water. The suspended solids play an extremely important role during the migration process. Figure 7 describes the effect of suspended solids concentration on heavy metal distribution.

As can be seen in Figure 3, the content of dissolved Hg in the aqueous phase increases with the amount of suspended matter, indicating that the resuspension of sediment is likely to cause secondary pollution of heavy metals. This further testifies that Hg mainly exists in granular state. In contrast, As content changes in the exactly opposite direction: it decreases with the increase of suspended matter. The trend might be attributable to its form of existence. With dissolved state as the dominant form of As in the water of the Jialing River, there is only a limited presence of the metal in sediment. This explains why the resuspension of sediment does not result in any increase in the content of dissolved As in the water.

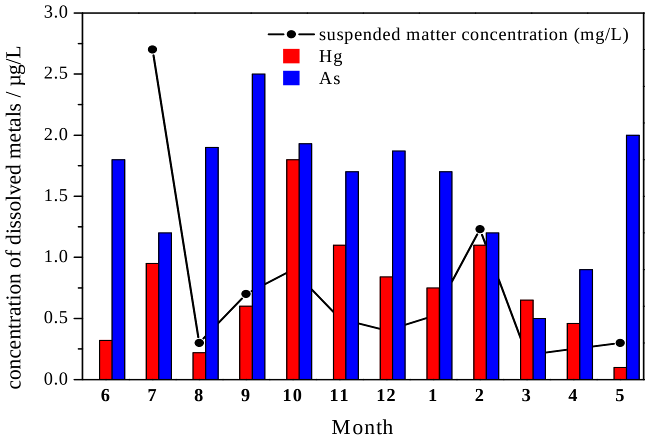

Figure 3: Relationship of suspended matter concentration and dissolved metal concentration

3.3 Enrichment of heavy metals in organisms

In the same animal group, the content of heavy metal varies with the type of heavy metal. For the same heavy metal, its content differs from animal group to animal group. Within the body of animal, different tissues are highly selective for different types of heavy metals. By virtue of their ability in the rapid synthesis of metallothionein in large quantities, the kidney and the liver are important target organs for heavy metal accumulation.

3.3.1 Distribution and enrichment of heavy metals in fish

Table 2 shows the measured contents of Hg and As in the six types of fish.

Table 2: Hg/As content of fish in the Jialing River

Fish	Length (cm)	Weight (g)	Flesh		Liver	
			Hg	As	Hg	As
S1	12.5	22.34	0.01(0%)	0.01(5.5%)	0.23(6.5%)	0.01(3.3%)
S2	14.7	35.64	0.01(0%)	0.01(6.0%)	0.51(6.3%)	0.01(1.2%)
S3	22.4	57.46	0.02(0%)	0.00(0%)	0.58(6.1%)	0.011(5.1%)
S4	13.0	29.76	0.06(8.7%)	0.02(5.1%)	0.40(7.2%)	0.07(4.1%)
S5	10.2	16.08	0.31(7.8%)	0.05(4.4%)	1.10(6.1%)	0.01(4.1%)
S6	26.4	305.00	0.03(6.6%)	0.01(7.2%)	0.45(6.3%)	0.01(4.1%)
S7	/	/	0.08(7.7%)	0.02(5.6%)	0.54(6.4%)	0.04(3.5%)

Except for Acrossocheilus monticola, none of the fish surpasses the food hygiene limits imposed on Hg (0.3mg/Kg) or As (0.5mg/Kg) by China. During the transmission along the biologic chain, the content of Hg increases with the trophic level. Being an omnivorous fish with a relatively short food chain, Carassius auratus has relatively low contents of Hg and As. With longer food chains, c

Carnivorous fishes like Acrossocheilus monticola feature relatively high contents of the two heavy metals.

With the exception of Pseudobagrus emarginatus, all the other five types of fishes exceed the limit on Hg content in fish liver; none of fish liver samples contains more than 0.5mg/Kg of As. Moreover, the liver enriches significantly higher levels of Hg and As than the flesh due to its physiological characteristics.

The Hg and As enrichment coefficients of the fish are acquired by the following formula: each enrichment coefficient = the average heavy metal concentration in fish samples / the average heavy metal concentration in water. It is calculated that the Hg and As enrichment coefficients of fish flesh are 230.3 and 7.5, respectively. Both coefficients are greater than 1, indicating the existence of Hg and As enrichment in the flesh. Plus, the Hg enrichment is more significant than As enrichment in fish flesh. Similarly, it is obtained that the Hg and As enrichment coefficients of fish liver are 1,636.4 and 19.7, respectively. Thus, it is deducted that the liver enriches significantly higher levels of Hg and As than the flesh. The result is consistent with the findings in other water bodies (Nasrin and Alim, 2015; Cannistraro et al., 2016; Cascetta et al. (Nasrin and Alim, 2015; Cannetraro et al., 2016; Cascetta et al., 2016).

3.3.2 Evaluation of heavy metal pollution in the fish

The potential health risks of the fish are assessed by target hazard quotients (THQs). There is no significant health risk when the THQ <1. The THQ is calculated by the following formula:

$$THQ=(E_F E_D F_{IR} C)/(R_{FD} W_{AB} T_A)\times 10^{-3} \quad (1)$$

Where E_F is the exposure frequency (365 days/year; E_D is the exposure duration (70 years), equivalent to human average life expectancy; F_{IR} is the food intake rate (g/person/day; C is the metal content in food (μg/g; R_{FD} is the reference dose (mg/kg/day; W_{AB} is the average body weight (55.9kg for each adult; T_A is the non-carcinogenic average exposure time t (365 days/year × 70).

The residents of Chongqing are divided into high, medium and low-income groups. Their daily fish consumption rates are 26.2, 15.7 and 7.6 g/person/day, and the reference doses of Hg and As are 5×10^{-4}mg/kg/day and 3×10^{-4}mg/kg/day, respectively. The calculated THQs are listed in Table 3.

Table 3: THQs of fish eating

Group	Metal content in flesh (μg/g)		THQ	
	Hg	As	Hg	As
High income	0.11	0.12	0.10	0.19
Middle income	0.01-0.29	0.01-0.41	0.06	0.11
Low income			0.03	0.05

From the above table, it is seen that As poses more latent risk than Hg in fish eating. In terms of THQ, neither of the two heavy metals surpasses 1, meaning that the risk is insignificant and the fish in the water body is safe to eat.

4. Conclusion

a. The average concentrations of dissolved As and Hg in the water samples are 1.55 and 0.64μg/L, respectively. The As concentration meets the standard for Class I water, and the Hg concentration satisfies the standard for Class IV water. The degree of Hg pollution is lightly polluted and that of As pollution is clean.
b. The content of dissolved Hg in the aqueous phase is significantly higher in the downstream than the upstream. The growing trend is caused by the gradual increase of plant effluents and domestic wastewater from tourism development along the flow direction of the river.
c. In the flesh of the fish caught from the Jialing River, both the Hg content or the As content fall below the food hygiene limits imposed by China. Among the tissues in fish body, the liver generally enriches more Hg and As than the flesh.
d. The fish in the Jialing River bears insignificant latent health risks, and As poses more risk than Hg in fish eating.

Acknowledgements

We would like to thank the National Natural Science Foundation of China (No. 51409049) for financial support.

Reference

Alonso E., Santos A., Callejón M., Jiménez J.C., 2004, Speciation as a screening tool for the determination of heavy metal surface water pollution in the guadiamar river basin. Chemosphere, 56(6), 561-70, DOI: 10.1016/0045-6535(94)90094-9.

Bai J., Xiao R., Zhang K., Gao H., 2012, Arsenic and heavy metal pollution in wetland soils from tidal freshwater and salt marshes before and after the flow-sediment regulation regime in the yellow river delta, china. Journal of Hydrology, s450–451, 11, 244-253, DOI: 10.1016/j.jhydrol.2012.05.006.

Bhosale U., Sahu K.C., 1991, Heavy metal pollution around the island city of bombay, india. part ii: distribution of heavy metals between water, suspended particles and sediments in a polluted aquatic regime. Chemical Geology, 90(3–4), 285-305, DOI: 10.1016/0009-2541(91)90105-z.

Burrows I.G., Whitton B.A., 1983, Heavy metals in water, sediments and invertebrates from a metal-contaminated river free of organic pollution. Hydrobiologia, 106(3), 263-273, DOI: 10.1007/bf00008125.

Cannistraro G., Cannistraro M., Cannistraro A., Galvagno A., 2016, Analysis of airpollution in the urban center of four cities Sicilian, International Journal of Heat and Technology, 34(2), 219-225. DOI: 10.18280/ijht.34S205.

Cascetta F., Musto M., Rotondo G., Barbato L., 2016, The influence of the fillingpercentage traffic on required ventilation thrust in road tunnel, International Journal of Heat and Technology, 34(2), 451-457. DOI: 10.18280/ijht.34S237.

Gümgüm B., Unlü E., Tez Z., Gülsün Z., 1994, Heavy metal pollution in water, sediment and fish from the tigris river in turkey. Chemosphere, 29(1), 111-116., DOI: 10.1016/0045-6535(94)90094-9.

Lozano J., Santos J.P., Suárez J.I., Herrero J.L., Aleixandre M., 2016, Detection of pollutants in water using a wireless network of electronic noses, Chemical Engineering Transactions, 54, 157-162, DOI: 10.3303/CET1654027

Ismail A., Toriman M.E., Juahir H., Zain S.M., Habir N.L., Retnam A., 2016, Spatial assessment and source identification of heavy metals pollution in surface water using several chemometric techniques. Marine Pollution Bulletin, 106(1–2), 292-300, DOI: 10.1016/j.marpolbul.2015.10.019.

Kozhenkova S.I., Khristoforova N.K., Chernova E.N., 2000, Long-term monitoring of sea water pollution by heavy metals in northern primorye with the use of brown algae. Russian Journal of Ecology, 31(3), 211-215, DOI: 10.1007/bf02762825.

Krishna A.K., Satyanarayanan M., Govil P.K., 2009, Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: a case study from patancheru, medak district, andhra pradesh, india. Journal of Hazardous Materials, 167(1–3), 366-373, DOI: 10.1016/j.jhazmat.2008.12.131.

Nasrin R., Alim M.A., 2015, Thermal performance of nanofluid filled solar flat platecollector, International Journal of Heat and Technology, 33(2), 17-24. DOI: 10.18280/ijht.330203.

Prasanna M.V., Praveena S.M., Chidambaram S., Nagarajan R., Elayaraja A., 2012, Evaluation of water quality pollution indices for heavy metal contamination monitoring: a case study from curtin lake, miri city, east malaysia. Environmental Earth Sciences, 67(7), 1987-2001, DOI: 10.1007/s12665-012-1639-6.

Sharifi Z., Hossaini S.M.T., Renella G., 2016, Risk assessment for sediment and stream water polluted by heavy metals released by a municipal solid waste composting plant. Journal of Geochemical Exploration, 169, 202-210, DOI: 10.1016/j.gexplo.2016.08.001.

Shirkhanloo H., Shirkhanloo N., Moussavinajarkola S.A., Farahani H., 2015, The evaluation and determination of heavy metals pollution in edible vegetables, water and soil in the south of tehran province by gis. Archives of Environmental Protection, 41(2), 64-74, DOI: 10.1515/aep-2015-0020.

Zhao S.Y., Su X.S., Zhao S.Y., 2016, A study on the water pollution of poultry and livestock breeding and the resource utilization of the wastewater in sonln village, Chemical Engineering Transactions, 55, 469-474, DOI: 10.3303/CET1655079