

Spatial distribution and speciation of mercury and methyl mercury in the surface water of East River (Dongjiang) tributary of Pearl River Delta, South China

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Abstract

Purpose The distribution and speciation of mercury in surface water of East River, Guangdong province, China were investigated.

Methods All told 63 water samples were collected during a bi-weekly sampling campaign from July 15th to 26th, 2009.

Results Total mercury (THg) concentrations in water samples ranged from 11 to 49 ng/L. Maximum levels of THg were measured in the lower reaches of East River, where it passes through a major industrial area adjacent to Dongguang city. Higher ratios of dissolved mercury (THg (aq)) in proportion to THg were restricted to the downstream section of East River. Concentrations of the minor constituent methyl mercury varied in the range from 0.08 to 0.21 ng/L. On average, methyl mercury made up 0.8% and 0.56% of THg (aq) and THg, respectively. Dissolved species dominated the speciation of methyl mercury in proportions up to 81%, which may imply that methyl mercury is largely produced in situ within the river water. Environmental factors (such as water temperature, dissolved oxygen, etc.) are

regarded to play an important role in Hg methylation processes were monitored and assessed.

Conclusions In an international perspective, East River must be classified as a polluted river with considerably sources within its industrial areas. The THg (aq) and particle mercury fluxes to the Pearl River Estuary by East River runoff were estimated to be 0.31 ± 0.11 and 0.17 ± 0.13 t/year, respectively. Hence, in total nearly 0.5 t Hg is annually released to the sea from the East River tributary.

Keywords Speciation · Mercury · Methyl mercury · Surface water · Pearl River delta · East River

1 Introduction

Mercury (Hg) is regarded as a global pollutant because of its high toxicity, persistency in the environment, and capability to undergo long-range transport in the atmosphere (Fitzgerald et al. 1998; Johansson et al. 2001; Wiener et al. 2006). In aquatic systems, inorganic Hg can be converted into organic Hg, especially methyl mercury (MeHg), which is biomagnified and bioaccumulated in aquatic food webs (Boudou and Ribeyre 1997; Goto and Wallace 2009) and this creates potential health risks to aquatic life and humans. Mercury methylation processes are controlled by chemical, physical and biological parameters, such as temperature, pH, redox potential, dissolved oxygen, dissolved organic matter and availability of Hg (Ullrich et al. 2001; Langer et al. 2001). Release of mercury to coastal zones and estuary systems by riverine systems has a significant impact on the local biogeochemical cycling of the metal (Paller et al. 2004; Molisani et al. 2007). A number of studies have surveyed the Hg loading and composition in major rivers of Europe and North America

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(Lawson et al. 2001; Domagalski et al. 2004; Faganeli et al. 2003; Schäfer et al. 2006), while the corresponding parameters of major rivers in Asia are still largely unknown. There is an urgent need to investigate Hg loading in major rivers globally to better constrain the cycling of Hg in the oceans (Mason et al. 1994).

East River (Chin. *Dong Jiang*) is one of three major tributaries of the Pearl River system, which in turn constitutes the largest river catchment of Southern China. East River is of comparatively short length (562 km) but includes a watershed area of about 27,040 km² (Zhang et al. 2009a), accounting for ~6% of the Pearl River system. The average annual runoff of East River is in turn 24×10^9 m³, accounting for 7.1% of the Pearl River system. East River crosses from Jiangxi Province through the eastern part of Guangdong province on its way to the Pearl River Estuary and eventually into the proper South China Sea, and serves as a major source of potable water for 40 million inhabitants in Guangdong province, Shenzhen special economic zone and Hong Kong special administration area. Following the rapid economic development in the Pearl River Delta (PRD) region, industrial activities, and domestic sewage by an increasing population have resulted in excessive discharge of pollutants into tributaries of the PRD (Ho et al. 2003) including mercury from metallurgical refinery as well as from manufacturing of chemicals, paints, electroplating, enamelware and batteries. A few studies have carried out to investigate the distribution of pollutants such as persistent organic pollutants (Fu et al. 2003), heavy metals and pathogenic micro biota (Ip et al. 2007) in the Pearl River and East River (Ho and Hui 2001; Ho et al. 2003). The status of Hg distribution in East River is to the best of our knowledge unexamined by the scientific community, although recently a study of the spatial distribution of this metal in sediments of Pearl River estuary has been published (Shi et al. 2010). The aim of the present work was to study the distribution and speciation of surface water Hg and MeHg along the full extent of East River to pinpoint pollution source regions and eventually to estimate its contribution to the input flux of Hg into the Pearl River Estuary.

2 Methods

2.1 Study area

The upper reach of East River constitutes essentially of a single channel while in its lower reach, downstream Dongguan city, the largest manufacturing base of electronic products in PRD, a complex river drainage is formed including a number of tributaries (see Fig. 1). In its upper reach section, surface water of East River was sampled at

14 locations denominated Z_i with highest three indices within the upstream Huizhou (HZ) region and the rest within Heyuan (HY) region. For the parallel channels of East River within the Dongguan (DG) region and downstream, the withdrawal point of raw water for Hong Kong/Shenzhen including all told 49 sampling sites, a classification from north to south is used for indication: A (nine sites), B (five sites), C (eight sites), D (eight sites) and E (19 sites). Channel segment A is proximate to Xintang municipality, which has numerous industries producing textile and clothing, mechanical parts, plastic, paper, printing and dyeing applications. Channel B flows through Mayong, a heavy industry base in the DG region including several industrial boilers and power plants. Adjacent to channel C is numerous chemical plants, paper mills, and clothing and toy factories. The major industrial activities surrounding channel D consist of textile and clothing, paper mills, plastic, medicine, glass, hardware, electronic, and mechanical factories. Segment E is most approximate to DG city area, which is a base of high-tech industries oriented towards optical electronics, medicine and information technology.

2.2 Sampling

Water samples were collected about 50 cm below surface using Pyrex glass bottles in a consecutive order from downstream to upstream of the river. The sampling was conducted during one biweekly campaign in the end of July (15th–26th) 2009. All sampling glass bottles were cleaned rigorously by immersion in diluted oxidising acid (10% HNO₃) followed by rinses with Milli-Q water. Subsequently, the bottles were heated in a muffle furnace at 500°C to remove mercury, doubled bagged after cooling and stored in the dark until employment. Initially during the river sampling, the bottles were rinsed three times with surface water before being filled. Both filtered and unfiltered water samples were collected for analysis. A filtered sample was obtained after passing through 0.45- μ m cellulose acetate membrane filter (Millipore, Germany). The filtration was performed on site. All collected samples were stabilised by addition of hydrochloric acid (ultra pure) to yield a 0.4% solution. Subsequently, all samples were stored in a portable cooler in the dark before being transported to the laboratory and conserved in a refrigerator at 4°C.

2.3 Analysis

In each water sample, temperature, pH, conductivity, salinity, dissolved oxygen content (DO), redox potential (ORP) as well as chloride, chlorophyll a (Chl-*a*), nitrate (NO₃⁻), and ammonium (NH₄⁺) concentrations were monitored in situ by using a portable water quality analyser (6600EDS, YSI company, USA).

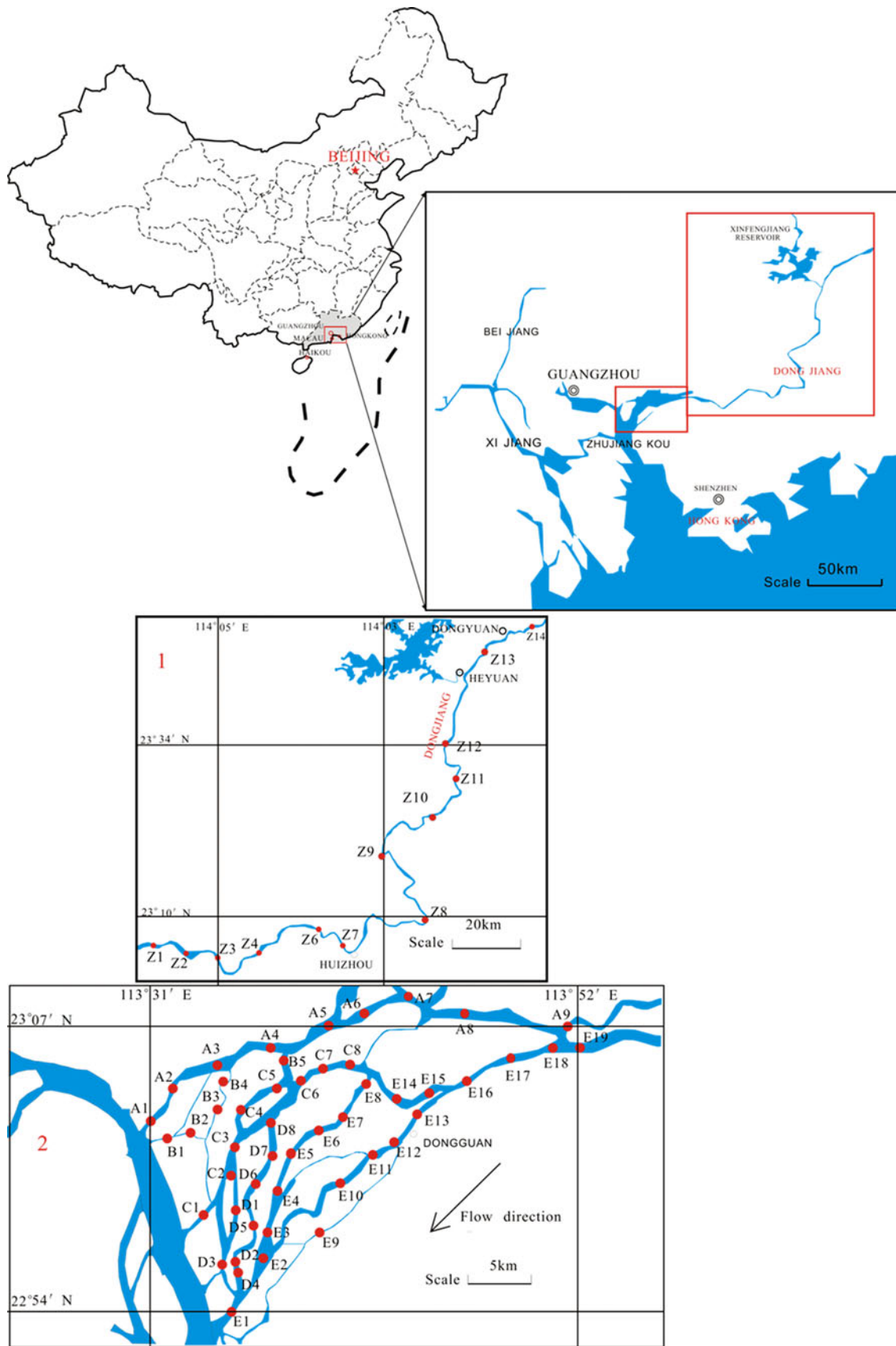


Fig. 1 Location of sampling stations in East River

The water samples were analysed for the following mercury species/fractions:

- Reactive Hg (RHg; $\text{Hg}^0(\text{aq})$ and labile $\text{Hg}^{\text{II}}(\text{aq})$ complexes reducible by SnCl_2). The RHg fraction includes labile species prone to undergo red-ox cycling and methylation (Rolfhus and Fitzgerald 1995). The RHg concentration (unfiltered samples) was determined by cold vapour atomic fluorescence spectroscopy (CVAFS, Tekran 2500 analyser, Tekran Instruments Corp, USA) after reduction with SnCl_2 and preconcentration on a gold trap.
- Total Hg in unfiltered samples (THg) and in filtered samples (THg (aq)) were determined by CVAFS following the procedures of United States Environmental Protection Agency (USEPA) Method 1630 (2001).
- Particulate Hg (PHg) was determined indirectly by subtracting THg (aq) from THg. Methyl mercury in unfiltered samples (MeHg) and in filtered samples (MeHg (aq)) were analysed by CVAFS after distillation, ethylation and isothermal GC separation procedures (Liang et al. 1994; USEPA Method 1631 (1999)).
- Quality assurance/quality control measures to assess the analytical processes included field blanks, method blanks, sample duplicates, spike recoveries, and the application of certified reference materials. The average \pm standard deviation of field blanks was 0.27 ± 0.06 and 0.035 ± 0.012 ng/L for THg and MeHg, respectively. The relative standard deviation for duplicate sample analysis was $<10\%$ for both THg and MeHg. The recovery of standard spikes was within 85–120% for MeHg and within 90–116% for THg, respectively. A certified reference material (ORMS-4, National Research Council Canada) was utilised during the THg analysis. Statistical data treatment was executed by using SPSS 16.0 for Windows software (SPSS Inc., Chigaco, IL, USA).

3 Results

3.1 East River water quality evaluation

A basic statistical assessment of the water quality parameters is given in Table 1. As can be seen East River is slightly alkaline (the mean pH value is 7.8 ± 0.25) with a low salinity level (the mean salinity is 0.09 ± 0.03 mg/L).

Chl-*a*, widely used as a proxy of the plant biomass in water (Hamilton and Schladow 1997), was present in a concentration range from 0.33 to 17 $\mu\text{g/L}$. Along the whole reach of East River, the NO_3^- concentration was elevated

(mean concentration, 7.7 mg/L) which by far exceed the USEPA drinking water standard of 1 mg/L (USEPA 1992). Peak concentrations of nitrogen constituents NH_4^+ and NO_3^- (maxima of 4.5 and 22 mg/L, respectively) of were measured at points C2 and Z13, approximate to discharges of untreated sewage.

3.2 The distribution and speciation of Hg

3.2.1 Hg in river system

Concentrations of RHg, THg (aq), PHg, THg in water samples were as summarised in Table 2. THg (aq) was highest elevated in channel C (16 ± 3.7 ng/L), whereas minimum concentrations (6.3 ± 2.2 ng/L) were measured in the HZ area section of East River (Table 2). The River channel C is adjacent to chemical plants that use Hg as a catalyst to produce acetic acid. A large amount of Hg was consumed by those chemical plants and these plants may also discharged wastewater contained elevated Hg concentrations to the environment (Jiang et al. 2006; Feng et al. 2009). Hg-contaminated wastewater is also discharged into East River section C resulting in Hg contamination. On the whole, from upstream (HY and HZ area) to downstream (DG area) of East River, THg (aq) exhibits an increase trend, which mimics that of RHg. Consequently, a significant positive correlation ($r=0.524$, $p<0.01$, $n=62$) could be established between RHg and THg (aq). THg also shows a significant correlation ($r=0.482$, $p<0.01$, $n=62$) with THg (aq) indicating a common origin (Faganelli et al. 2003).

The THg level measured (19 ± 3.1 ng/L) never exceed the international drinking water standard for total Hg (6,000 ng/L; WHO 2008) as well as the maximum level allowable for drinking water for total Hg (50 ng/L) defined by Ministry of Environmental Protection of China (CN-EPA 2002; Fig. 2). However, THg concentrations in water at all sampling sites exceeded the 12 ng/L USEPA standard for Hg to protect against chronic effects to aquatic life (USEPA 1992) as indicated in Fig. 2. Moreover, THg concentrations in East River significantly exceeded levels that are considered uncontaminated in rivers of North America and Europe (1–3 ng/L (Gill and Bruland 1990); <5 ng/L (Ullrich et al. 2001)). In terms of surface water Hg levels, the contaminated C channel section of East River compares favourably with Baihua reservoir in Guizhou province, which is contaminated by Hg containing discharges of an organic chemical plant, with slightly lower mean THg concentration (24 vs. 36 ng/L) but with higher concentration of RHg (8.4 vs. 5.7 ng/L; Yan et al. 2003). Hence, several sections of East River exhibit Hg contamination, whereby the deteriorated water quality posing a hazard to adjacent

Table 1 Interval and mean values ± standard deviation of the studied parameters in water samples from East River

Area	DG					HZ	HY
	A	B	C	D	E		
River channel ID Sampling sites	A1–A9	B1–B5	C1–C8	D1–D8	E1–E19	Z1–Z11	Z12–Z14
Temperature (°C)	30±0.28	31±0.31	31±0.56	32±0.17	31±0.44	30±0.42	30±0.77
Conductivity (mS/cm)	0.29±0.06	0.28±0.09	0.24±0.04	0.28±0.03	0.20±0.04	0.12±0.03	0.10±0.003
Salinity (mg/L)	0.12±0.03	0.12±0.04	0.10±0.02	0.12±0.01	0.08±0.02	0.05±0.01	0.04±0
Dissolved oxygen (mg/L)	3.7±0.06	3.7±0.02	2.5±1.7	2.8±1.2	2.1±1.4	6.0±1.5	7.5±0.55
pH	7.85±0.07	7.83±0.11	7.72±0.19	7.99±0.11	7.66±0.16	7.90±0.33	8.13±0.46
Redox potential (mV)	-273±5.28	-261±15	-250±22	-232±28	-264±22	-267±14	-268±7.5
Cl ⁻ (mg/L)	100±24	90±31	72±22	92±33	65±31	29±15	18±2.93
NH ₄ ⁺ (mg/L)	4.1±0.28	3.9±0.33	3.6±0.61	3.8±0.33	3.1±0.49	3.3±0.40	3.6±0.40
NO ₃ ⁻ (mg/L)	7.6±0.18	5.5±2.15	4.3±2.7	2.6±0.60	7.0±1.9	12.4±2.7	18.1±3.1
Chlorophyll- <i>a</i> (µg/L)	4.1±0.39	5.5±1.73	5.4±3.0	14.6±1.8	4.9±3.7	1.2±1.0	1.3±1.4

ecosystems and populations using it as it posed a great drinking water resource.

3.2.2 MeHg in river system

In all segments from East River, MeHg concentrations in surface water were present in the range 0.08–0.21 ng/L (mean, 0.14±0.05 ng/L; Table 2). None of the water samples contained elevated levels of MeHg (≥1 ng/L); however, MeHg is significantly bioavailable and therefore accumulated in fish. Consequently, low MeHg in the bulk water may be compatible with high MeHg levels in predator fish in the same water mass (da Silva et al. 2005). The phase distribution of observed MeHg is in favour of the dissolved species (MeHg (aq)) with a proportion up to 81%. In addition, concentrations of MeHg and MeHg (aq) are statistically significant ($r=0.704$, $p<0.01$, $n=63$) linear correlated. Therefore, it may be hypothesised that MeHg is produced in situ within East River.

4 Discussion

4.1 Spatial patterns of mercury distribution along East River

The proportion of THg (aq) relative to THg was slightly lower in the HZ (~37%) compared to the HY area (42%) but increased again downstream in the multi river channel delta within DG area, where section E turned out to contain lower ratios (~53%) than the rest of the parallel channels (~65–70%). This may originate in a divergence in the Hg source pattern along the river. Three zones could thus be identified including a heavy industrialised zone of DG area (A–D sites), a largely urbanised zone around Dongguan city (E sites) and a less industrialised zone around the upper reach of East River (Z sites).

Using one-way analysis of variance, it was concluded that THg (aq) data lumped into the three zone categories showed larger variation between groups ($F=22.967$, $p<0.001$). The THg(aq) concentration ($9.0±1.7$ ng/L) in

Table 2 The statistical summary of different Hg species in surface water samples collected from East River (ng/L)

Area	River Section	RHg		THg (aq)		PHg		THg		MeHg		MeHg (aq)	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Dongguan (DG)	A1–A9 (A)	8.4	2.2	12	2.2	5.9	4.4	17	3.4	0.095	0.028	0.050	0.044
	B1–B5 (B)	6.3	1.3	15	6.1	8.2	2.6	24	4.4	0.14	0.028	0.079	0.061
	C1–C5 (C)	6.9	2.6	16	3.7	8.0	7.3	24	10	0.19	0.085	0.16	0.072
	D1–D8 (D)	8.3	2.6	13	3.9	5.5	5.2	18	3.6	0.21	0.054	0.12	0.068
	Total (A–D)	7.5	2.4	14	4.5	6.9	5.1	21	6.7	0.16	0.071	0.10	0.080
	E1–E19 (E)	4.9	0.88	9.0	1.7	8.0	4.8	17	3.8	0.21	0.12	0.14	0.070
Huizhou(HZ)	Z1–Z11	4.0	2.4	6.3	2.2	11	5.5	17	5.7	0.10	0.050	0.046	0.025
Heyuan(HY)	Z12–Z14	2.3	1.6	7.9	5.9	11	10	19	5.0	0.077	0.017	0.043	0.021
East River overall		5.8	2.5	11	4.6	8.3	5.4	19	5.8	0.06	0.093	0.095	0.070

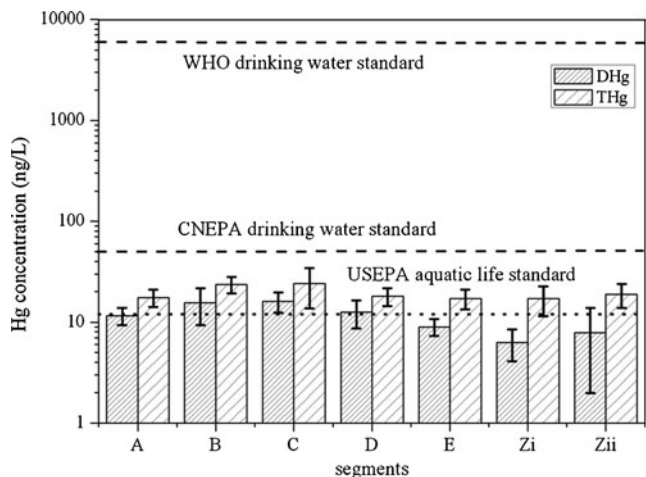


Fig. 2 THg and THg (aq) concentrations from seven segments in East River

sections A–D (Table 2) is within the range of levels reported in other heavily impacted and industrialised areas, such as in the Sepetiba Bay tributaries, SE Brazil (Paraquetti et al. 2004) and in the Narragansett Bay tributaries, USA (Vandal and Fitzgerald 1995). River channel segment E lacks obvious industrial sources of Hg contamination. In this zone, the source of Hg discharges to the river may be mainly domestic sewage, coal combustion and also possibly automobile emissions. The upper reaches of East River are dominated by input from agricultural activities, whereby exhibiting maximum concentration level of NO_3^- as an indicator of watershed runoff (Table 1). Moreover, the PHg level observed in East River of the HY and HZ region (HY, 11 ± 10 ng/L; HZ, 11 ± 5.5 ng/L) were significantly higher than that in DG area (6.9 ± 5.1 ng/L) possibly indicating the effect of soil erosion (Table 1).

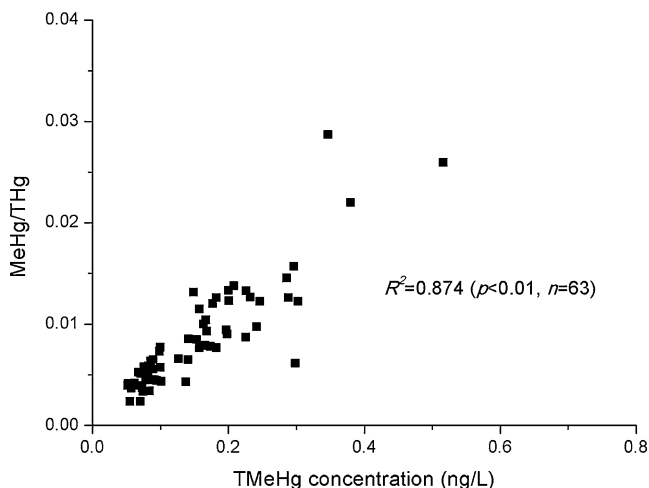


Fig. 3 The correlation between MeHg and MeHg/THg in water in East River

Table 3 Pearson's correlation matrix, giving the linear correlation coefficients (*r*) between the variables

	RHg	THg (aq)	PHg	THg	MeHg (aq)	MeHg	DO	pH	ORP	Cl ⁻	NH ₄ ⁺	NO ₃ ⁻	Chl- <i>a</i>	T
RHg	1													
THg (aq)	0.524**	1												
PHg	-0.175	-0.324*	1											
THg	0.223	0.472**	0.668**	1										
MeHg(aq)	0.065	0.040	0.078	0.092	1									
MeHg	0.231	0.136	0.113	0.202	0.656**	1								
DO	-0.412**	-0.401**	0.186	-0.144	-0.472**	-0.460**	1							
pH	-0.126	-0.285*	0.235	-0.041	-0.288*	-0.222	0.655**	1						
ORP	0.079	0.154	-0.011	0.072	0.154	0.125	-0.031	0.147	1					
Cl ⁻	0.415**	0.213	0.051	0.140	0.457**	0.347**	-0.462**	-0.114	0.337*	1				
NH ₄ ⁺	0.204	0.193	-0.100	0.040	-0.276*	-0.342**	0.254	0.408**	0.300*	0.345**	1			
NO ₃ ⁻	-0.421**	-0.426**	0.225	-0.096	-0.401**	-0.355**	0.626**	0.277*	-0.453**	-0.563**	-0.172	1		
Chl- <i>a</i>	0.407**	0.226	-0.228	-0.069	0.268*	0.321*	-0.384**	0.208	0.487**	0.560**	0.312*	-0.615**	1	
T	0.334*	0.443**	-0.167	0.168	0.411**	0.430**	-0.508**	-0.108	0.525**	0.443**	0.176	-0.830**	0.652**	1

* $P < 0.05$
 ** $P < 0.01$

4.2 MeHg production

To investigate MeHg production, we followed the procedures by several studies to calculate %MeHg used as a surrogate measurement for methylation activity (Mitchell et al. 2008; Zhang et al. 2009b). Firstly, ratios of MeHg to THg were calculated ranging from 0.2% to 3%, with an average of $0.9 \pm 0.5\%$. There is a significant positive correlation ($r=0.935$, $p<0.01$, $n=63$) between MeHg and MeHg/THg in waters (Fig. 3). This suggested that there is a strong potential of methylation of Hg in East River. Secondly, there is a substantial pool of RHg in proportion to that of THg in the water samples ($30 \pm 15\%$), which is substantially higher than that of MeHg in relation to THg. This indicates a high potential for mercury in East River to undergo red-ox transformation and other conversion such as methylation.

MeHg production in aquatic system has been examined to be influenced by a wide variety of environmental factors, such as the availability of Hg, ORP, DO, water temperature, presences of inorganic and organic solutes as well as microbial activity (Ullrich et al. 2001). To investigate the possible controlling factors, the correlation matrix between Hg species/fractions and eight water quality parameters measured (DO, pH, ORP, Cl^- , NH_4^+ , NO_3^- , Chl-*a* and temperature) is tabulated (Table 3). As can be seen in Table 3, with the exception of pH and ORP, the remaining six water parameters were found to be significantly correlated with MeHg in the river system. T, Cl^- , and Chl-*a* were significantly positively correlated with MeHg concentration, while DO, NH_4^+ , and NO_3^- were significantly negatively correlated with MeHg concentration.

4.3 Hg loading from East River into South China Sea

Riverine input forms an important source of Hg entering the South China Sea (Fu et al. 2010). The THg (aq), THg, and PHg concentration in surface water were highly elevated in downstream including A, B, C, D and E segments (Table 2). The annual discharge of East River is $24 \times 10^9 \text{ m}^3$. Using these data, the average fluxes of THg, THg (aq), and PHg to the South China Sea by East River were estimated to be 0.48 ± 0.14 , 0.31 ± 0.11 and 0.17 ± 0.13 t/year, respectively. As the average annual runoff of East River accounts for 7.1% of the Pearl River, the riverine input fluxes of THg, THg (aq) and PHg to the South China Sea by the Pearl River were estimated to be 6.8 ± 2.0 , 4.4 ± 1.6 and 2.4 ± 1.8 t/year. In an oceanographic study of the North South China Sea, Fu et al. (2010) used a limited number of THg sampling data from the PRD ($\sim 40 \text{ ng/L}$) to predict corresponding flow of ~ 34 t/year into the Sea. However, in a perspective, our data of mercury load to the South China Sea by the Pearl River are higher than, e.g., that of Yalu River to the Northern Yellow Sea by in China (2.6

and 1.5 t/year of THg and THg (aq) respectively; Liu 1999), and the Hg fluxes in the Sepetiba Bay tributaries, SE Brazil (0.011 t/year of THg (aq) and 0.19 t/year of THg; Paraquetti et al. 2004).

In the effort to scale up our East River Hg data to yield estimates of annual Hg runoff of the Pearl River catchment into the Sea, the data temporal limitation and lack of information from the remaining tributaries compelled us choosing a very simple approach. The calculation was based on the assumption that there was no seasonal variation in Hg concentration in East River and that this parameter is levelled out to represent the whole catchment. In the Pearl River system, West River (Chin. *Xi Jiang*) and North River (Chin. *Bei Jiang*) are the largest tributaries, whose average annual runoff account for 70.8% and 11.7% of the total, respectively. More data on riverine inputs were required to quantify the riverine influxes to South China Sea. First of all, Hg concentrations in surface water of three large tributaries of the Pearl River both in wet and dry season need to be measured. Moreover, Hg concentrations in eight mouths of the Pearl River system in different season need also be studied.

5 Conclusions

Our data indicated elevated levels of both THg and MeHg in surface water in East River when compared to rivers in pristine areas in North America and Europe. An increase trend of THg (aq) concentrations from the upstream to the downstream of the river was observed. The majority of TMeHg was present as dissolved species MeHg (aq), which implies that MeHg is produced within East River bulk. This study highlights that the elevated levels of THg (aq) in surface water in industrial zone of DG area are a consequence of industrial and domestic sewage inputs. The Pearl River system is an important source of Hg input into the South China Sea.

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