HEAVY METALS IN SUSPENDED SEDIMENTS IN RIVERS FLOWING THROUGH MEGACITIES IN SOUTHEAST ASIA

Chihiro Yoshimura[1], Chikako Yamanaka[2], Manabu Fujii[3],
Suchat Leungprasert[4], and Maria Antonia Tanchuling[5]

[1] Tokyo Institute of Technology, Tokyo, Japan, e-mail: yoshimura.c.aa@m.titech.ac.jp
[2] Tokyo Institute of Technology, Tokyo, Japan, e-mail: yamanaka.c.aa@m.titech.ac.jp
[3] Tokyo Institute of Technology, Tokyo, Japan, e-mail: fujii.m.ah@m.titech.ac.jp
[4] Kasetsart University, Bangkok, Thailand, e-mail: fengscl@ku.ac.th
[5] University of the Philippines, Manila, Philippines, e-mail: maria_antonia.tanchuling@upd.edu.ph

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Abstract

Heavy metals in suspended sediments (SS) were investigated in the lower Chao Phraya River, Thailand, and Marikina-Pasig River basin, Philippines, both in the rainy and dry seasons. In addition, we assessed the relative pollution level of SS by determining enrichment factor of particulate metals. The particulate fractions accounted mostly for 60-100% of total concentrations of Cr, Mn, Ni, Cu, Zn, and Pb in both dry and rainy seasons. The comparison of metal contents of the sampled SS and upper continental crust (UCC) implied some anthropogenic inputs of Cr, Ni, Cu, and Zn as well as the dilution process for those metals in the rainy season in Chao Phraya River. Enrichment factor in both rivers also indicated anthropogenic effects on metal content in SS, reflecting the distinctive seasonal process in Chao Phraya River and the spatial variation within Marikina-Pasig River basin. Overall, the results revealed the importance of the particulate phase of heavy metals in both target rivers to understand the transport and reactivity of heavy metals.

Keywords: Chao Phraya river, Enrichment factor, Heavy metals, Marikina-Pasig river, Suspended sediments

Introduction

In Southeast Asia, heavy metals are being accumulated in urban rivers, estuaries, and adjacent coastal zones (Prudente et al., 1994; Urase et al., 2006; Thongra-ar et al., 2008; Zhu et al., 2010) as one of the consequences of the recent rapid urbanization and industrialization. Bioavailability and toxicity of heavy metal depend on its concentration as well as chemical speciation. For example, zinc and copper are essential for the growth of organisms, while its accumulation in aquatic organisms results in the inhibition of a number of processes involved in metabolic pathways (e.g., Spencer and Nichols, 1983; Di Toro et al, 2001). Thus, heavy metals can negatively affect aquatic organisms and ecosystems, depending on their concentration and chemical speciation, which highlights the importance of proper monitoring and management of heavy metals in aquatic systems.

Several large rivers in Southeast Asia are also characterized by a massive load of suspended sediments (SS) (Meybeck et al., 2003). Such high sediment load is largely the result of natural processes (e.g., erosion and transport) in their catchments and often makes water quality control complex in terms of water supply as well as ecological management. Consequently, the deterioration of aquatic ecosystems is closely related to SS in highly turbid rivers because SS serves as the carrier of a number of pollutants including heavy metals, causing secondary and tertiary pollutions in adjacent water bodies (Urase et al., 2006; Zhu et al., 2010), and SS can be also potential food sources for aquatic fauna.

In highly turbid rivers, therefore, it is required to monitor heavy metals both in dissolved and particulate phases because heavy metals are likely to present mostly in particulate phase and such particulate metals can be leached out and drastically increase its toxicity, depending on the physicochemical condition of water. Thus, it is important to investigate heavy metal property in SS to understand those sources, transport processes, and potential risk in rivers and coastal area. However, such properties of heavy metals in SS have been rarely investigated in Southeast Asia, although the metal accumulations in bottom sediments are often reported in rivers, estuaries, and adjacent coastal zones (Prudente et al., 1994; Urase et al., 2006; Thongra-ar et al., 2008; Zhu et al., 2010).

In this study, therefore, we focused on urban rivers of two megacities in Southeast Asia: Bangkok in Chao Phraya River basin and Greater Manila in Marikina-Pasig River basin. In those rivers, heavy metals in dissolved and particulate phases were examined both in the rainy and dry season. Further, we assessed the relative pollution level of SS by determining enrichment factor of particulate metals.

Target Area

Surface water was collected at 9 sites along Chao Phraya River, Thailand and 10 sites in Marikina-Pasig River and its tributaries in Greater Manila, Philippines (Figure 1). In Chao Phraya River we covered the section from Chao Phraya Dam (277 km from the month) down to its month. In Marikina-Pasig River we also sampled the drainage from the dumping site at Payatas and San Juan River in addition to the major rivers. Chao Phraya River and Marikina-Pasig River have catchment areas of 160,400 km^2 and 570 km^2, respectively. Both rivers are substantially influenced by monsoon climate resulting in distinct seasonal patterns in hydrology. In addition, those rivers transport an enormous amount of fine sediments to the coastal area, and the river water is characterized by high turbidity especially in the rainy season.

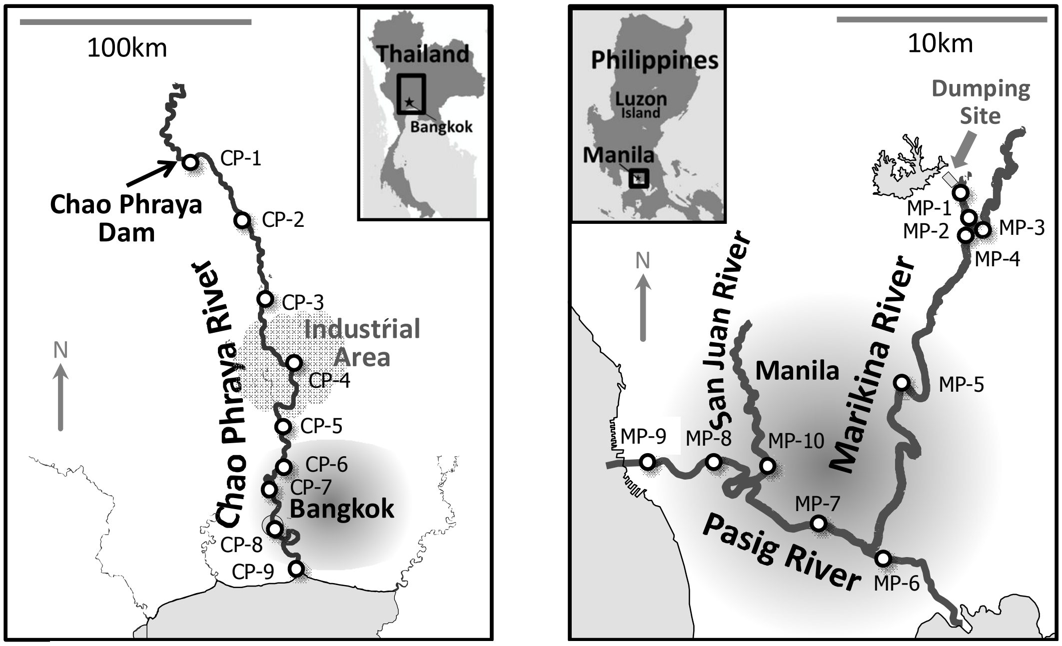

Figure 1. Target areas and sampling points in Chao Phraya River (Thailand) and Marikina-Pasig River (Philippines)

Methods

Water Sampling and Basic Water Quality

River water was sampled under stable discharge condition both in the rainy and dry seasons at the target sites along Chao Phraya River (2 August 2011, 20-21 January 2012) and Marikina-Pasig River (21 March 2012, 21-22 August 2012). At each sampling site, surface water (0.5-1.0 L) was collected from a bridge or river shore using acid-washed polyethylene bottles, and basic physicochemical parameters (water temperature, pH, electrical conductivity, dissolved oxygen (DO)) were determined. The sampled water was immediately transported to the laboratory and then filtered by Durapore membrane filter (0.22 μm, Millipore). Until analyzed, both the filtrate in bottles and SS retained on the filter were stored under dark and cool condition (4ºC). Dissolved organic carbon (DOC) was determined with TOC analyzer (TOC-5000A, Shimadzu). For the determination of SS concentration, the solids in water samples from Chao Phraya River and Marikina-Pasig River were separated by centrifugation (3,600 rpm, 30 min) and filtered by glass fiber filter (1.0 μm, Whatman), respectively, dried in an oven at 60°C for 24 hours, and then weighed.

Determination of Heavy Metals and Enrichment Factor

The metal concentrations in all the filtrates were analyzed by ICP-MS (Agilent 7700x) after adding HNO_3 (final concentration 1%) to the filtrates (detection limit: 0.3μg/L for Fe, < 0.1 μg/L for others). The target elements were Cr, Mn, Ni, Cu, Zn, Pb, and Fe. Others (As, Cd, Hg) were found to be below or near the detection limit for most of the samples. To estimate the pollution level of SS, total metal concentration was also determined after the digestion with 0.23 M HNO_3 and 0.57 M HCl (25°C for 12 h and 95°C for 4 h, respectively). Those results were then used to calculate total concentrations of particulate metals and enrichment factor (EF) of Cr, Ni, Mn, Cu, Zn, and Pb. EF is based on the ratio of a target element content to Fe contents:

$$EF = \frac{(Metal/Fe)_{sample}}{(Metal/Fe)_{UCC}} \tag{1}$$

where *Metal* and *Fe* are those contents (mass ratio) of the sample and the upper continental crust (UCC) (Wedepohl, 1999). Thus, EF can be considered as a concentration factor of heavy metal relative to the reference, which is UCC in this study.

Result and Discussion

Basic Water Quality and Heavy Metal Concentrations

SS concentrations were found to be in the range of 55-148 mg/L and 20-30 mg/L in the rainy and dry seasons respectively in Chao Phraya River, while they were 20-255 mg/L and 12-100 mg/L in the rainy and dry seasons respectively in Marikina-Pasig River (Figure 2). Those results indicate that both rivers are in a medium range in world major rivers in terms of SS concentration (Meybeck et al., 2003). Overall, SS concentrations were higher in the rainy season than those in the dry season at all the sites, except for the Pasig River (MP-7, 8), indicating that soil erosion and SS transport, due to precipitation, surface runoff, and increased discharge, result in high SS concentration. The water temperature ranged from 25.9 to 29.2°C and pH was neutral (7.17 – 7.91) among all the monitored sites. Electrical conductivity was within the range from 16.9 to 60.9 mS/m, except for the site in the month of Chao Phraya River (1,496 mS/m) and the drainage from Payatas dumping site

(137 – 149 mS/m). DO and DOC were found to be 4.7 – 7.7 mg/L and 4.3 – 7.2 mg/L, respectively in Chao Phraya River, showing no clear trend both in spatial and seasonal

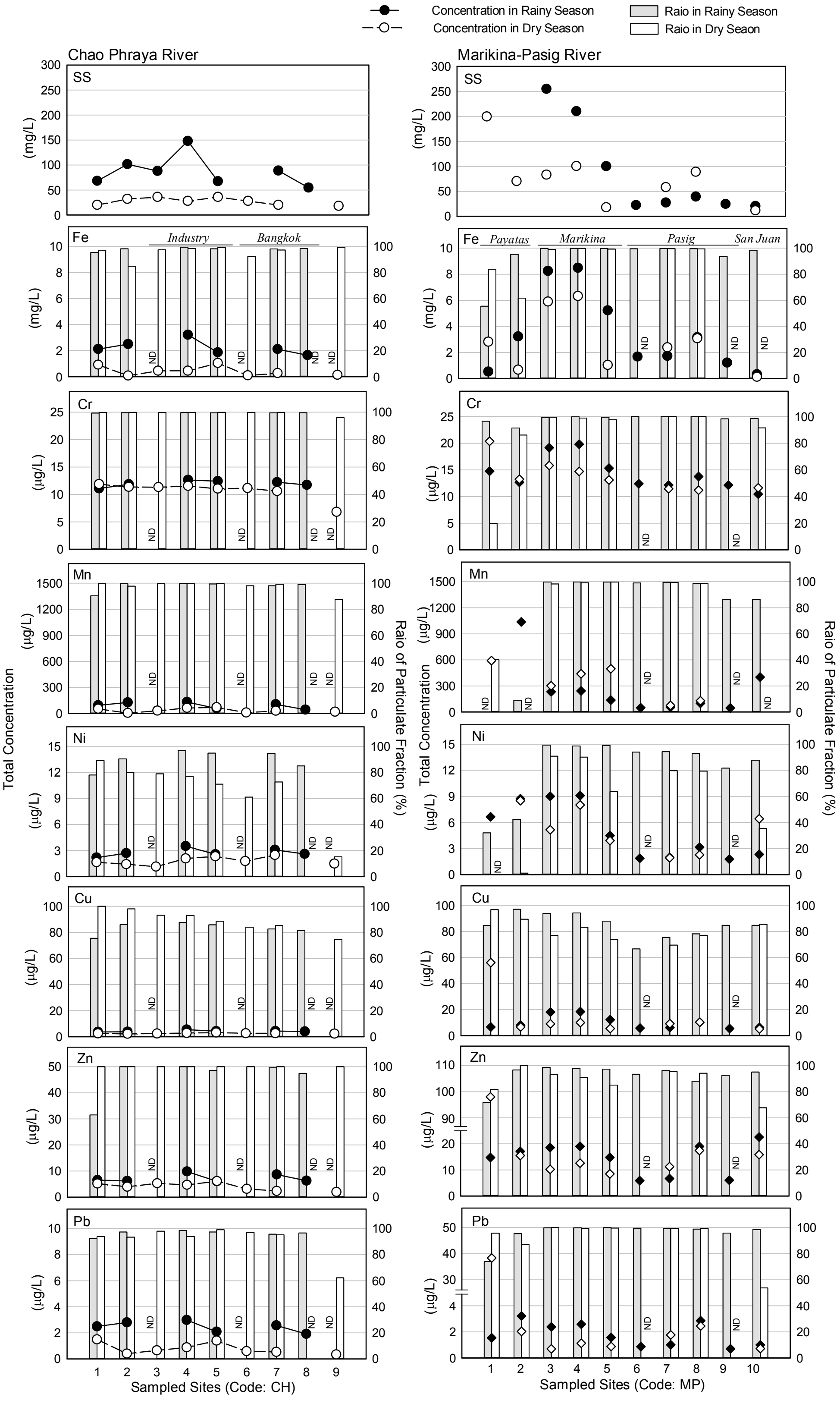

Figure 2. Total concentrations of SS and heavy metals (left axis) and ratio of particulate metal to total metal (right axis) in Chao Phraya River (left panels) and Marikina-Pasig River (right panels). ND: not determined

changes. In contrast, DO and DOC showed the high spatial variability in Marikina-Pasig River (DO 0 – 8.6 mg/L, DOC 2.9 – 1,188 mg/L), indicating organic pollution in the drainage from the dumping site as well as its dilution in Marikina and Pasig rivers especially in the rainy season.

The total metal concentrations in the target rivers were found to be in the ranges of 81–8,480 µg-Fe/L, 6.3–591 µg-Mn/L, and ~1–100 µg/L for Cr, Ni, Cu, Zn, and Pb. Overall, the metal concentrations in Marikina-Pasig River basin were similar to or higher than those in Chao Phraya River (Figure 2). The drainage from the dumping site (MP-1 & -2) in the dry season showed an order of magnitude higher concentration for Mn, Cu, Zn, and Pb compared to the other sites of Marikina-Pasig River. The rainy season showed higher total concentrations of all the six elements shown in Figure 2, compared to the dry season, at most of the sites in both rivers, while the ratios of particulate fraction were stable over two distinct seasons, except for Cd and Ni. The particulate fraction in the rivers, except for the drainage, accounted for more than 15% (mostly 60-100%) of total concentrations of Cr, Mn, Ni, Cu, Zn, and Pb in the dry season, while it was over 63% in the rainy season (Figure 2).

Heavy Metal Content and Enrichment Factor of Suspended Sediments

The heavy metal contents differed in the rainy and dry seasons in Chao Phraya River, whereas their variations highlighted the spatial characteristics of metal input to river sections in Marikina-Pasig River basin (Figure 3). Excluding the drainage from the dumping site, the contents were within the range of 57.6-911.2 µg/g for Cr, 192-4,340 µg/g for Mn, 3.7-193.6µg/g for Ni, 32.0-374.6 µg/g for Cu, 60.3-917 µg/g for Zn, and 8.3-73.4 µg/g for Pb. Enrichment factor (EF) also indicated seasonal and spatial patterns of pollution level of heavy metals in the sampled rivers. Overall, EFs of the six elements were found to be higher than 1, except for Ni at MP-2 (drainage) and Pb at MP-3, 4, and 5 (Marikina River), (1.7-78.8 on average, Figure 4). The results indicate the significant enrichment of heavy metals, relative to Fe content, in SS at most of the sampled sites. The highest EF in the sampled sites was found to be 145 for Cr in Chao Phraya River and 28.4 for Mn, 37.0 for Ni, 129 for Cu, 139 for Zn, and 28.2 for Pb in Marikina-Pasig River basin. The multi-element average of EF for each season and site ranged from 1.7 to 78.8 (Figure 4).

In Chao Phraya River, the contents of Cr, Ni, Cu, and Zn were apparently higher in the dry season than those in the rainy season, which was possibly exaggerated by the extraordinary flood in the rainy season in 2011 in Thailand. Given also the fact that the metal contents of SS sampled in this river are higher than UCC (Cr 35 µg/g, Ni 18.6µg/g, Cu 14.3µg/g, Zn 52 µg/g (Wedepohl, 1999)), our results implied some anthropogenic inputs of those heavy metals as well as the dilution process for those metals in the rainy season. In addition, EF indicated the peaks at CP-2 (47.5) and CP-6 (35.6) in the dry season while EF is generally higher in the dry season than in the rainy season (Figure 4). Thus, there might be some sources of heavy metal at upstream sections of those two sites and the input from those sources possibly increase EF in Chao Phraya River, which seems to be diluted by SS originated from natural system in the upper basin in the rainy season. More specifically, based on the local maps of river network, geology (Jumchet and Javanaphet, 1969), and land use (Department of Land Development, 1998), the reasonable sources for the peaks of EF at CP-2 and CP-6 are local geology and land use, respectively.

The tributaries coming into the section from CP-1 and CP-2 flow through catchments where Kanchanaburi and Ratburi formations are dominated and possibly characterized by high EF, whereas other tributaries in the downstream of CP-2 flow mostly on the plain of alluvium or eluvium (Jumchet and Javanaphet, 1969). The peak at CP-6 seems to be

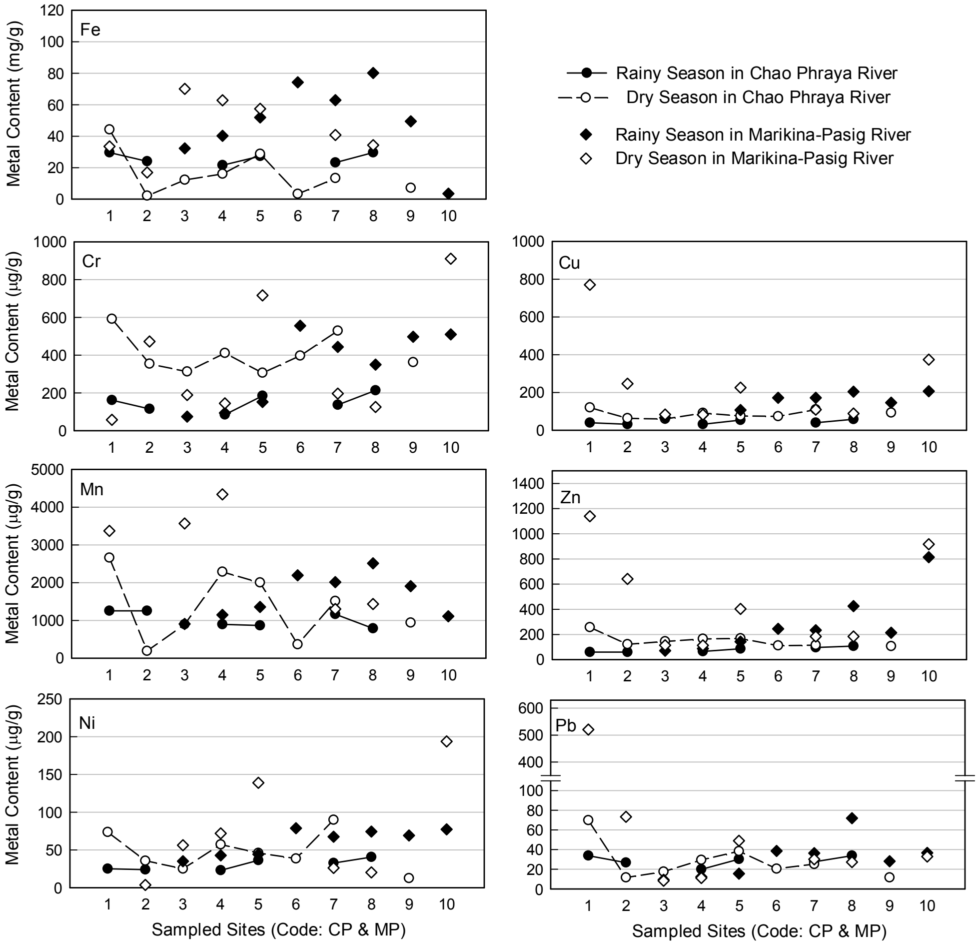

Figure 3. Metal contents in suspended sediments (SS) in Chao Phraya River (circles) and Marikina-Pasig River (rhombuses)

caused by scattered urbanized land (Department of Land Development, 1998) as there is no difference in local geology. In addition, the heavy metals seem to be more enriched in SS as the rivers receive less sediment supply from soil erosion and SS concentration becomes lower, typically in dry season, under such condition the anthropogenic effect on heavy metal dynamics becomes evident.

In Marikina-Pasig River basin, the drainage from the dumping sites (MP-1, 2) in the dry season showed exceptionally higher content of Cu (771.2 µg/g), Zn (1140 µg/g), and Pb (520 µg/g) than in other river section, while San Juan River (MP-10) was also characterized by high contents of Cr, Ni, and Zn. In addition, the high EF for Cr, Cu, Zn and Pb in the drainage from the dumping site (Figure 4) revealed that this site is one of the major sources of particulate metals in Greater Manila at least in the dry season, which corresponds to the high metal concentration levels (especially for Cu, Zn, and Pb) in the bed sediments reported for Pasig River and Manila Bay (Prudente et al., 1994; Urase et al., 2006). Interestingly, the contents of all the six elements were higher in the rainy season than in the dry season only in Pasig River (MP-7, 8) (Figure 3), indicating the unique processes of metal transport in the river, which is possibly the surface runoff from Manila city. Concerning Pb, the highest EF was found to be 28.2 (in dry season) in the drainage

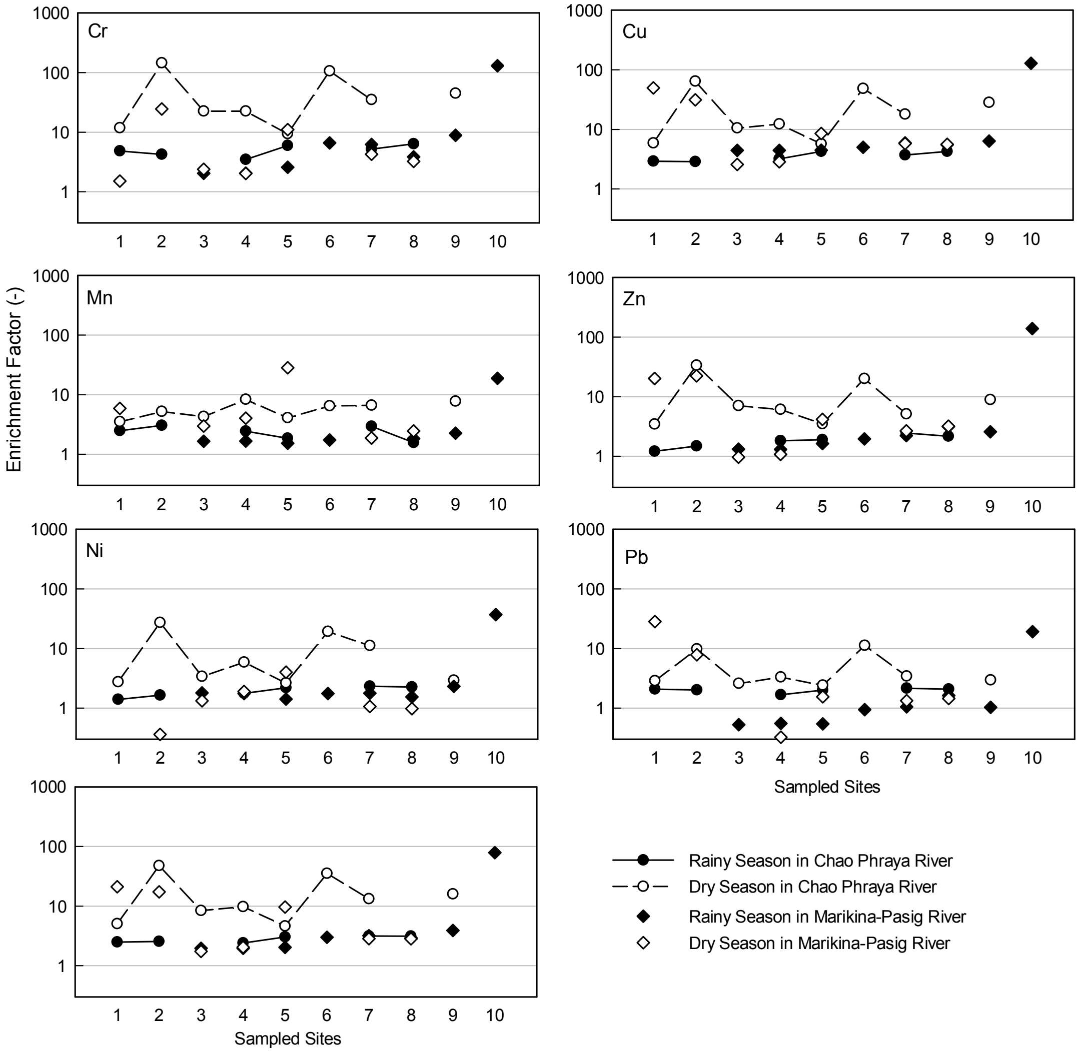

Figure 4. Enrichment factors (EF) of particulate heavy metals in the lower Chao Phraya River and Marikina-Pasig River

from the dumping site, which was slightly higher than those reported for the bottom sediments in South China Sea (Sc-based EF: 0.6 – 13.8 (Zhu et al., 2010)). The relatively high EF of Pb was observed in the area close to large cities and major river mouths (Zhu et al., 2010), and thus SS from urban rivers is dominant transporter of heavy metal to coastal areas in South China Sea. Those facts also imply a general trend of higher enrichment levels of Pb in SS, especially in the dry season, compared to those of bottom sediments in rivers and coastal area. In addition to those facts, the target area of Greater Manila is much smaller than that of Chao Phraya River, so the effect of human activities on heavy metal distribution could be more important compared to local geology in Greater Manila.

Overall, EF in the both rivers was found to be the similar range over 1, indicating anthropogenic and natural effects on SS property (e.g., heavy metal content). In addition, such apparent anthropogenic input of metal contained SS seems to reflect the distinctive seasonal process in Chao Phraya River and the spatial variation of river sections in Marikina-Pasig River basin, as shown in Figure 4. However, such spatio-temporal variation of EF did not clearly explain the seasonal difference, nor spatial distribution of concentrations of total and particulate metals, shown in Figure 2, except for the drainage from the dumping site. Nevertheless, these results reveal the importance of the particulate phase of heavy metals in both target rivers to understand the transport processes of heavy metals.

Correlation of Heavy Metals to Physicochemical Water Quality

We also applied simple correlation analysis for our results to understand better the relationship of particulate and dissolved phases of heavy metals within each river system, focusing on physicochemical parameters (water temperature, pH, DO, EC, and DOC) (Table 1, 2). In the lower Chao Phraya River, pH was correlated negatively to the concentration of dissolved Cu and Zn and also positively to the ratio of particulate Cu, showing the highest correlation coefficients (Table 1). Considering the facts that those metals were present predominantly in the particulate phase (Figure 2), the results from correlation analysis implies that pH is a significant factor determining dissolved concentration of metals, which is relevant to its bioavailability and toxicity, in the lower Chao Phraya River. Further, the bottom layer of the river is generally characterized by reducing condition and thus the solubility of heavy metals is possibly increased. At the same time, SS may have the buffering capacity of metals that is capable of reducing metal toxicity, for which further study is required.

In contrast, DOC concentration and EC showed significant correlations with several metals in case of Marikina-Pasig River basin (Table 2). DOC was found to be correlated positively with dissolved concentrations of Cr, Mn, Ni, and Zn and negatively with particulate ratios of Cr, Ni, Zn, and Pb. The correlation of pH and DO to dissolved metal concentration and particulate ratio were found to be lower than in Chao Phraya River, even though the range of pH was similar in the target rivers. The significant correlations of DOC and EC imply the simultaneous loading of organic matter and heavy metals, which is supported also by the high maximum concentration of DOC (16.1 mg/L) in this river basin. It is likely that those pollutants originate from the Payatas dumping site, domestic and industrial wastewater, and stormwater urban runoff as speculated by Urase et al. (2006).

Conclusions

Based on the results explained above, the major findings on heavy metals in SS in Chao Phraya River and Marikina-Pasig River basins can be summarized as follows:

- The total metal concentrations in the targeted rivers were found to be in the ranges of 81–8,480 µg-Fe/L, 6.3–591 µg-Mn/L, and ~1–100 µg/L for Cr, Ni, Cu, Zn, and Pb. The particulate fractions accounted mostly for 60-100% of total concentrations of Cr, Mn, Ni, Cu, Zn, and Pb in both dry and rainy season.
- The comparison of metal contents of the sampled SS and UCC implied some anthropogenic inputs of Cr, Ni, Cu, and Zn as well as the dilution process for those metals in the rainy season in Chao Phraya River.
- Enrichment factor (EF) in the rivers indicated anthropogenic effects on metal related property of SS, reflecting the distinctive seasonal process in Chao Phraya River and the spatial variation within Marikina-Pasig River basin. In addition, the high EF for Cr, Cu, Zn and Pb in the drainage from Payatas revealed that the dumping site is one of the major sources of particulate metals in Greater Manila at least in the dry season.

- In the lower Chao Phraya River, pH was correlated negatively to the concentration of dissolved Cu and Zn and also positively with the ratio of particulate Cu, whereas DOC concentration and EC showed significant correlations with several metals in case of Marikina-Pasig River basin.

Table 1. Correlation of Physicochemical Water Quality to Dissolved Metal Concentration and Ratio of Particulate Metal in Chao Phraya River (Including Both Rainy and Dry Seasons). The High Salinity Site was Excluded. The Number of Samples in this Correlation Analysis is 14 or 15 Except for Zn Concentration (n=4). * $0.01 < p \leq 0.05$, ** $p \leq 0.01$, - not Significant

		Temp. °C	pH	DO mg/L	EC mS/m	DOC mg/L
Range		27.4-29.2	7.3-7.9	4.6-7.7	16.9-29.7	4.3-7.2
Dissolved Metal Concentration (μg/L)						
Cr	0.01-0.28	-	-	-	-	-
Mn	0.13-9.15	-	-	-	-	-
Ni	0.11-1.25	-	-	-0.56 *	-	0.60 *
Cu	0.04-0.89	0.74 **	-0.75 **	-	-	-
Zn	0.06-3.66	-	-0.97 *	-	-	-
Pb	0.01-0.19	0.66 **	-	-	-	-
Ratio of Particulate Metal (%)						
Cr	96.0-99.9	-	-	-	-	-
Mn	87.4-99.7	-	-	-	-	-
Ni	15.3-96.9	-	-	-	-	-
Cu	74.4-100.0	-0.54 *	0.81 **	0.77 **	-	-
Zn	63.1-100.0	-	-	-	-	-
Pb	62.3-99.1	-	-	-	-	-

Table 2. Correlation of Physicochemical Water Quality to Dissolved Metal Concentration and Ratio of Particulate Metal in Marikina-Pasig River (Including Both Rainy and Dry Seasons). The Data from the Drainage from the Payatas Dumping Site are not Included in this Analysis and the Number of Samples in this Correlation Analysis is 13 or 14 Except for Cr Concentration (n=7). * $0.01 < p \leq 0.05$, ** $p \leq 0.01$, - not Significant

		Temp. °C	pH	DO mg/L	EC mS/m	DOC mg/L
Range		25.9-31.0	7.2-7.8	0.0-8.7	19.4-60.9	2.9-16.1
Dissolved Metal Concentration (μg/L)						
Cr	0.04-0.98	-	-	-	-	0.90 **
Mn	0.26-378.4	0.54 *	-0.54 *	-	0.59 *	0.61 *
Ni	0.04-4.14	-	-	-0.57 *	0.73 **	0.89 **
Cu	0.75-2.81	-	-	-	-	-
Zn	0.24-5.91	0.63 *	-0.56 *	-0.61 *	0.65 *	0.62 *
Pb	0.0-0.33	-	-	-	-	-
Ratio of Particulate Metal (%)						
Cr	91.6-100.0	-	-	-	-0.62 *	-0.77 **
Mn	86.5-99.8	-0.56 *	-	-	-	-
Ni	35.3-99.3	-	-	0.66 **	-0.76 **	-0.87 **
Cu	66.5-94.1	-	-	-	-	-

Zn	67.7-98.7	-	-	0.57 *	-0.65 *	-0.77 **
Pb	53.6-100.0	-	-	-	-	-0.71 **

Overall, the results revealed the importance of the particulate phase of heavy metals in both target rivers to understand the transport and reactivity of heavy metals, while the potential sources and seasonal dynamics seem to be different between the two urban areas, possibly depending on geological and hydrological conditions as well as environmental management in basins. To ensure the effective management on heavy metal toxicity, thus, it is important to further investigate the chemical speciation of particulate heavy metal and its relation to the leachability of heavy metal under various water quality conditions.

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