APN Science Bulletin
Issue 3, March 2013
ISSN 2185-761x

APN

ARCP2010-01CMY-STHIANNOPKAO

Trace Metal Contamination in Southeast Asian Rivers

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ABSTRACT: River water was collected from the Tonle Sap-Bassac Rivers (Cambodia), the Citarum River (Indonesia), the lower Chao Phraya River (Thailand) and the Saigon River (Viet Nam) in both dry and wet seasons. Nineteen trace metals were analysed (Be, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Ba, Tl and Pb). Dissolved metal concentrations of most target elements exceeded the background metal concentrations by multiples of 1.1 to 87.8. Cluster and stable lead isotope analyses confirmed metal contamination in Southeast Asian rivers is anthropogenically linked. For example, discharges of wastewater, road runoff and street dust. Quantitative risk assessments of metals in the rivers showed potential toxicity of additives and negative effects of metal mixtures at all sampling sites in all areas studied. The contribution of particular metals to the cumulative criterion units (CCU) score depended on their concentrations. Al in all study areas contributed the highest percentage (72% to 85%) to total CCU scores. Cd, Cr, Cu, Pb, Ni, Zn, As and Se had lower contributions (<1% to 19%).

KEYWORDS: *metals, rivers, risk assessment, urbanization, source tracking, Southeast Asia*

Introduction

Over the past four decades Southeast Asia (SEA) has witnessed rapid urbanization and population growth, accompanied by economic and industrial expansion. These have led to a fast-paced deterioration in the environment. Recent water quality monitoring programmes in several SEA countries have furnished data showing a severe deterioration in river water caused by a variety of pollutants, including suspended solids, nutrients, organic pollutants and pathogenic microorganisms (Marcotullio, 2007; Visvanathan & Padmasri, 2010; Evans et al., 2012). For trace metal contamination of river water, however, such data is not readily available, due to economic limitations and the lack of tools and techniques to accurately measure metal concentrations.

The objectives of this study on metal pollution were to i) determine the concentrations of trace metals in selected rivers of SEA, ii) identify the potential sources contributing trace metals into the rivers using a multivariate statistical approach and stable isotope analysis, and iii) assess the potential environmental risks of metal contamination to aquatic organisms using cumulative criterion units (CCU).

Methodology

Water samples were collected from five selected rivers flowing through four main urban centres of SEA: the Tonle Sap-Bassac Rivers of Phnom Penh (Cambodia), the Citarum River of Bandung (Indonesia), the lower Chao Phraya River of Bangkok (Thailand) and the Saigon River of Ho Chi Minh City (Viet Nam). Two river water sampling campaigns were conducted to collect representative samples in both dry and wet seasons. All sampling points located along the river course, from both upstream and downstream, were selected to represent the whole urban area (Figure 1).

The concentrations of 19 trace metals were determined by inductively coupled plasma mass spectroscopy (ICP-MS; Agilent 7500ce) and inductively coupled plasma optical emission spectroscopy (ICP-OES; Perkin Elmer Optical 5300DV). In addition, four lead isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, in the water samples were also measured using the ICP-MS (Agilent 7500ce).

The SPSS software package was used to perform all statistical analyses on the database. A cluster analysis (CA) was applied to group the sampling sites into categories or clusters on the basis of similarities within a cluster and dissimilarities between different clusters, with respect to distance between objects. In addition, to identify sources of lead contamination using a graphical method, the results of the four lead isotopes in the water samples were compared to various composition sources and natural background levels obtained from the literature.

Results and Discussion

Since surveys of dissolved metal concentrations in natural waters in SEA have received relatively little attention (Gaillardet et al., 2003), the world average dissolved metal concentrations of uncontaminated

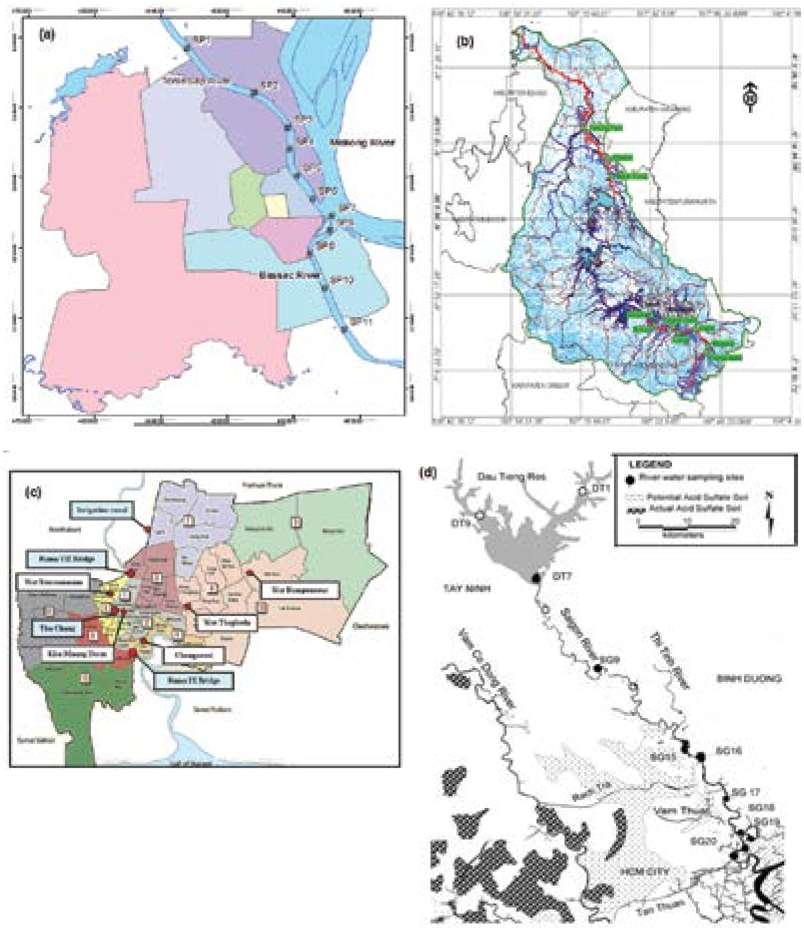

Figure 1. Maps show sampling site locations along the (a) Tonle Sap-Bassac Rivers (Cambodia), (b) Citarum River (Indonesia), (c) lower Chao Phraya River (Thailand) and (d) Saigon River (Viet Nam)

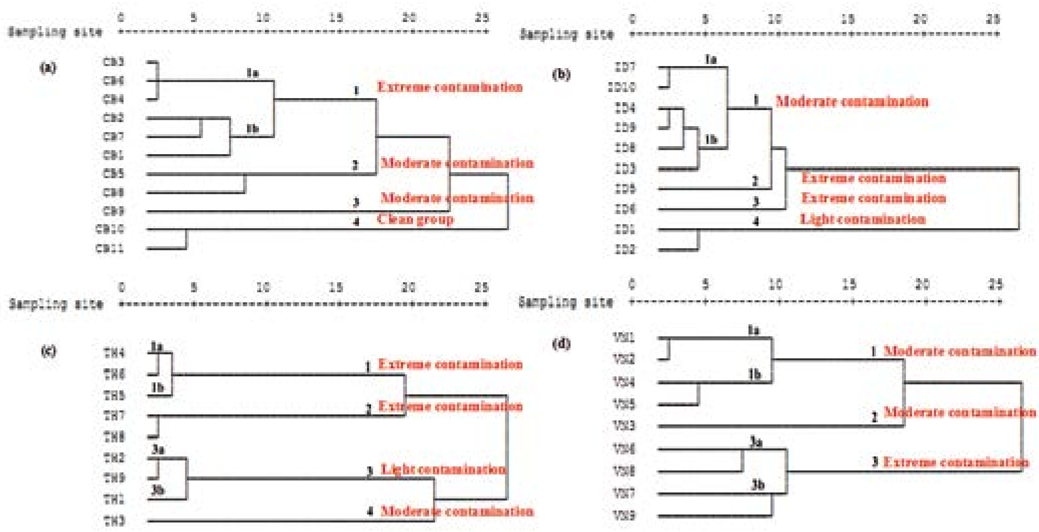

Figure 2. Dendrograms showing spatial similarities of monitoring sites in the (a) Tonle Sap-Bassac Rivers, (b) Citarum River, (c) lower Chao Phraya River and (d) Saigon River

rivers were used in this study to assess the degree of metal contamination; the natural background dissolved concentrations are not especially different among river systems (Luoma & Rainbow, 2008). Utilizing such an approach, Sindren et al. (2007) had concluded that anthropogenic enrichment of metals in a river system could be revealed by metal concentrations that exceeded the range of background concentrations.

The results of dissolved metal concentrations among the areas studied (Table 1) revealed that the Tonle Sap-Bassac Rivers were contaminated only with V and As. The Citarum River, the lower Chao Phraya River, and the Saigon River were contaminated with most metals of interest. Dissolved metals and the multiples of their background concentrations in this study were Al (1.9 to 3.0), Ti (2.5 to 5.6), V (1.2 to 5.4), Cr (1.3), Mn (1.1 to 5.7), Fe (1.6 to 3.9), Co (3.1 to 3.6), Ni (1.8 to 8.2), Cu (1.5 to 2.8), Zn (16.7 to 87.8), As (1.1 to 5.7), Mo (1.2 to 4.1), Cd (2.5 to 10.9), Ba (1.4 to 8.4) and Pb (5.5 to 7.1).

To help identify the likely sources of metal contamination in river water, cluster analysis (Figure 2) was used to categorize all monitoring sites in each area studied into several clusters, according to the sites' similarities in metal concentrations. This produced clusters labeled "clean", "light contamination", "moderate contamination" and "extreme (heavy) contamination."

The results of a scatter plot of stable lead isotope data ($^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$) (Figure 3) clearly revealed that anthropogenic sources are the major cause of Pb contamination in these Southeast Asia

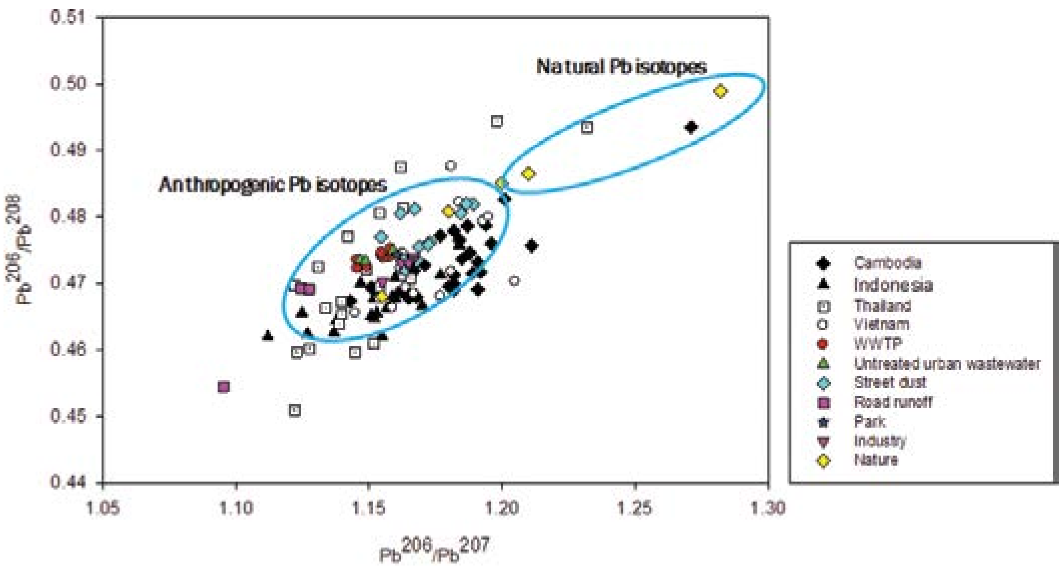

Figure 3. $^{206}Pb/^{207}Pb$ ratio as a function of $^{206}Pb/^{208}Pb$ in river waters of Southeast Asia countries (Cambodia, Indonesia, Thailand, and Viet Nam) compared with several sources of Pb pollution reported in previous studies

Study area		Be	Al	Ti	V	Cr	Mn	Fe	Co	Ni
Cambodia (Tonle Sap-Bassac Rivers)	Min.	ND	ND	ND	0.67	0.10	ND	ND	0.01	ND
	Max.	ND	34.61	0.72	1.29	0.46	4.15	22.76	0.16	0.56
	Median	-	7.98	0.33	**0.83**	0.30	0.43	10.96	0.03	0.33
Indonesia (Citarum River)	Min.	ND	18.28	0.51	1.67	ND	6.89	17.65	0.19	0.17
	Max.	0.06	291.20	13.36	8.38	2.80	638.00	557.40	1.25	9.66
	Median	0.01	**96.59**	**2.75**	**3.84**	0.79	**195.10**	**193.35**	**0.47**	**1.45**
Thailand (Lower Chao Phraya River)	Min.	ND	32.25	ND	1.22	0.43	ND	ND	0.08	3.94
	Max.	0.50	267.83	1.32	2.64	6.49	1189.0	409.60	2.89	23.54
	Median	0.16	**61.82**	0.48	**2.46**	**1.16**	**38.89**	**105.60**	**0.54**	**6.57**
Viet Nam (Saigon River)	Min.	ND	5.99	0.09	0.24	0.01	9.03	7.59	0.08	ND
	Max.	0.08	2507.0	5.77	3.04	8.98	179.80	2590.0	1.30	3.90
	Median	0.00	**70.04**	**1.24**	**1.55**	**1.13**	**72.49**	**258.08**	**0.50**	**2.26**
World average (as background concentrations)		NA	32.00	0.49	0.71	0.85	34.00	66.00	0.15	0.80

Table 1. Concentrations of dissolved metals (µg L^{-1}) in Southeast Asia rivers

rivers. It was found that both point sources (wastewater treatment plants, power stations) (Figure 4(a)) and non-point sources (atmospheric wet deposition, street runoff, street dust, automobile exhaust) (Figure 4(b)) were significant contributors of Pb into river waters. Natural Pb concentrations from sediment and seawater were found at some sampling sites in Thailand and Viet Nam. Stable Pb isotopic ratios found in this study were not close to those of the natural Pb components.

For the quantitative assessment of trace metal contamination in Southeast Asia rivers, a quantitative risk evaluation (Figure 5) showed that CCU scores greater than 1 were found at all sites on the Tonle Sap-Bassac Rivers, the Citarum, the lower Chao Phraya, and the Saigon River. Figure 5 indicates the chronic, additive and unsustainable negative effects of metal mixtures in those river systems on aquatic organisms. The CCU scores for the Tonle Sap-Bassac, the Citarum, the lower Chao Phraya, and the Saigon rivers in the dry season varied from 8.1 to 29.5, 134.1 to 433.5, 1.2 to 3.4 and 22.3 to 180.5, respectively. The CCU scores at the same sites on the Tonle Sap-Bassac Rivers and the lower Chao Phraya in the wet season were higher than in the dry season by an average multiple of 13.9 and 2.4 (Figures 5(a) and 5(c)), respectively. In contrast, the CCU scores for the Citarum River were generally about 3.1 times higher in the dry season than in the wet (Figure 5(b)). The CCU scores for the Saigon River in the wet season were highly varied, from 13.2 to 140.0, and were not usually higher than the CCU scores at the same sampling sites in the wet season (Figure 5(d)). Interestingly, it was found that the contribution of each metal to the CCU score can change depending on its concentration. Aluminium (Al), a non-priority pollutant, in all areas studied contributed about 72% to 94.1% to total CCU scores. The other elements, including Cd, Cr, Cu, Pb, Ni, Zn, As and Se, generally had relatively lower contributions to total CCU scores (<1% to 19%). Therefore, among all metals, Al may exhibit greatest toxicity to aquatic organisms.

HIGHLIGHTS

- Rivers in four Southeast Asia countries were contaminated with various trace metals.
- Non-point sources of metals in the rivers were from road runoff and street dust.
- Point sources of metals were from wastewater discharge.
- Metal contamination poses chronic and additive effects on aquatic microorganisms.
- Aluminium may present highest toxicity for aquatic organisms.

Conclusions

Rivers in four SEA countries were found to be contaminated with various heavy metals. Anthropogenic sources, including non-point (road runoff and street dust) and point sources (discharge of industrial and household wastewater) were the major contributors of

Study area		Cu	Zn	As	Se	Mo	Ag	Cd	Ba	Tl	Pb
Cambodia (Tonle Sap-Bassac Rivers)	Min.	0.25	ND	0.69	ND	0.02	ND	ND	2.34	ND	ND
	Max.	1.62	ND	3.46	0.12	1.21	ND	ND	15.13	0.01	0.17
	Median	1.06	-	**1.57**	0.00	0.21	-	-	5.03	0.00	0.02
Indonesia (Citarum River)	Min.	0.51	3.28	0.52	0.04	0.20	ND	ND	7.07	ND	0.10
	Max.	6.94	44.26	5.55	0.63	0.95	0.26	0.06	68.14	0.09	1.30
	Median	**2.23**	**10.02**	**2.25**	0.17	**0.69**	0.04	0.02	**32.37**	0.04	**0.44**
Thailand (Lower Chao Phraya River)	Min.	1.12	28.06	2.24	ND	0.72	ND	ND	104.40	ND	0.32
	Max.	14.22	160.60	5.23	0.68	3.25	2.50	0.32	255.50	0.30	1.88
	Median	**4.23**	**52.69**	**3.53**	0.21	**1.71**	0.20	**0.20**	**203.30**	0.15	**0.54**
Viet Nam (Saigon River)	Min.	0.55	5.38	0.24	ND	0.08	ND	0.20	9.28	ND	ND
	Max.	16.51	311.10	1.26	0.61	1.43	2.24	245.00	33.08	0.03	6.55
	Median	**3.23**	**49.53**	**0.69**	0.00	**0.52**	0.09	**0.87**	19.71	0.00	**0.57**
World average (as background concentrations)		1.50	0.60	0.62	NA	0.42	NA	0.08	23.00	NA	0.08

Table 1. Concentrations of dissolved metals (µg L^{-1}) in Southeast Asian rivers (cont.)

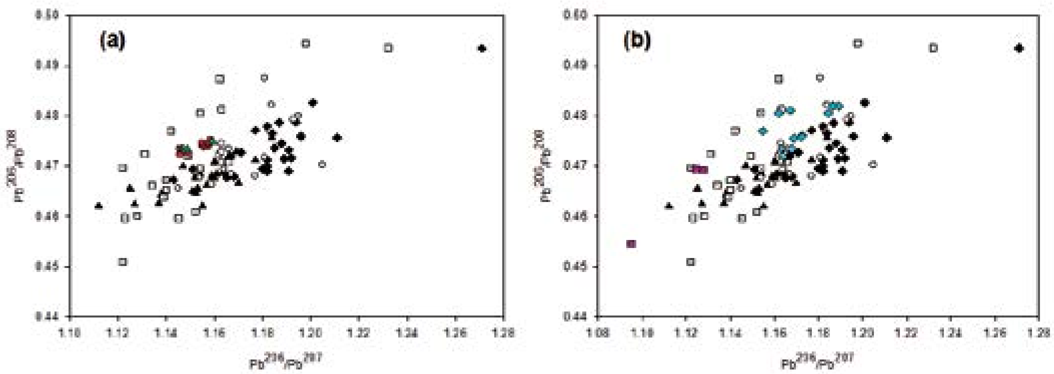

Figure 4. $^{206}Pb/^{207}Pb$ ratio as a function of $^{206}Pb/^{208}Pb$ in river waters of Southeast Asian countries (Cambodia, Indonesia, Thailand, and Viet Nam) compared with Pb pollution reported in (a) urban wastewater and (b) street dust and runoff obtained from previous studies

metal pollution in the rivers. Risk evaluation of metal toxicity using CCU scores clearly indicated the likelihood of additive and negative effects of metal pollution upon aquatic organisms in the study areas.

Acknowledgements

This research was financially supported by the Asia-Pacific Network for Global Change Research (ARCP2010-01CMY-Sthiannopkao), and Gwangju Institute of Science and Technology, Republic of Korea.

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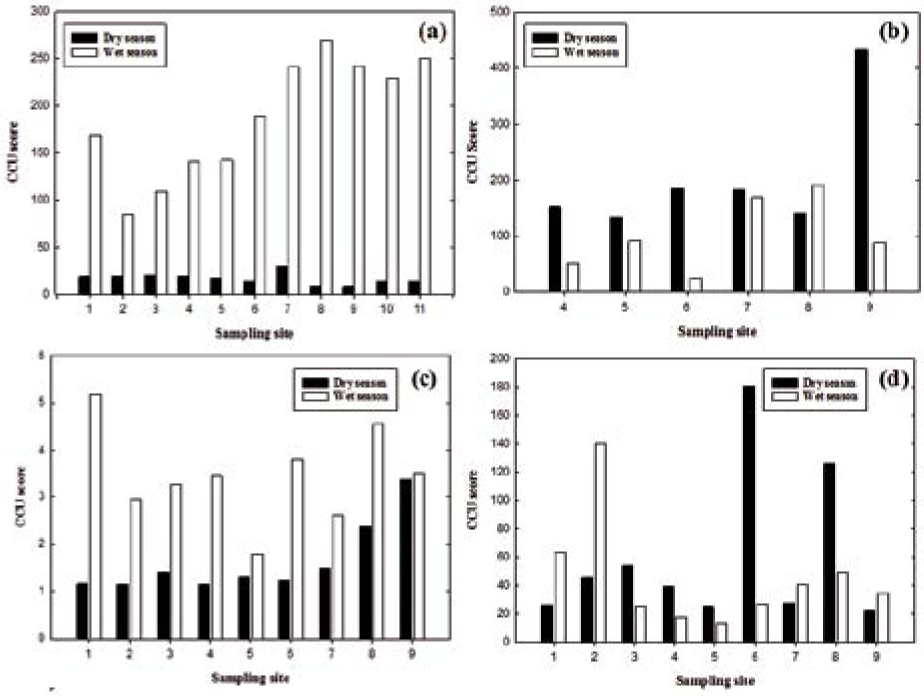

Figure 5. Quantitative risk evaluation of potential toxicity of metal mixtures in (a) Tonle Sap-Bassac Rivers, (b) Citarum River, (c) lower Chao Phraya River and (d) Saigon River

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ARCP2010-01CMY-STHIANNOPKAO

PROJECT TITLE

Collaborative Research on Sustainable Urban Water Quality Management in Southeast Asian Countries: Analysis of Current Status (Comparative Study) and Strategic Planning for Sustainable Development

COUNTRIES INVOLVED

China, Cambodia, Indonesia, Republic of Korea, Thailand , Viet Nam

PROJECT DURATION

2 years

APN FUNDING

US$ 80,000

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