ENVIRONMENTAL QUALITY BENCHMARKS FOR PROTECTING AQUATIC ECOSYSTEMS

Status of metal levels and their potential sources of contamination in Southeast Asian rivers

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Abstract To assess the concentration and status of metal contaminants in four major Southeast Asian river systems, water were collected from the Tonle Sap–Bassac Rivers (Cambodia), Citarum River (Indonesia), lower Chao Phraya River (Thailand), and Saigon River (Vietnam) in both dry and wet seasons. The target elements were Be, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Ba, Tl, and Pb and the concentrations exceeded the background metal concentrations by 1- to 88-fold. This distinctly indicates enrichment by human urban area activities. The results of a normalization technique used to distinguish natural from enriched metal concentrations confirmed contamination by Al, Cd, Co, Mn, Ni, Pb, and Zn. Cluster analysis revealed the probable source of metals contamination in most sampling sites on all rivers studied to be anthropogenic, including industrial, commercial, and residential activities. Stable lead isotopes analyses applied to track the sources and pathways of anthropogenic lead furthermore confirmed that anthropogenic sources of metal contaminated these rivers. Discharges of wastewater from both industrial and household activities were major contributors of Pb into the rivers. Non-point sources, especially road runoff and street dust, also contributed contamination from Pb and other metals.

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Introduction

Economic growth, expanding industrialization, rising populations, and rapid urbanization in Southeast Asia (SEA) over the past four decades have led the region to face an escalating deterioration in its environment. Water constitutes an immense part of this environment, a part whose condition many nations are trying to come to grips with. The importance of rivers to the economies and cultures of these regions of Asia can scarcely be exaggerated; they are as the lifeblood. Degraded water quality has inflicted various water-related burdens on communities. In addition to sanitation issues, there are such problems as water scarcity and inconsistent, unpredictable availability (Marcotullio 2007).

The uncontrolled releases of domestic sewage, industrial discharges, and agricultural and urban runoff are the major sources of river water contamination and continue to threaten the aquatic environments of many rivers in the SEA region (Evans et al. 2012). The growing use of water quality monitoring programs in this region has come to reveal a severe deterioration in river water brought on by several types of pollutants, including suspended solids, nutrients, organic pollutants, and pathogenic microorganisms (Marcotullio 2007; Visanathan and Padmasri 2010; Evans et al. 2012). While there is increasing availability of information and scientifically sound data on the state and trends of rivers from such common measures of river water quality as temperature, suspended solids, chemical oxygen demand, biochemical oxygen demand, and fecal coliform bacteria, the data on metal concentrations in river water is not readily available in this region. This is due fundamentally to

the economic limitations on the agencies involved, and more specifically to the lack of tools and techniques for the accurate measurement of metal concentrations, especially those of trace elements.

Metal contamination in river systems has become a major environmental quality issue for many rapidly growing SEA cities because the infrastructure for water production, quality, and sanitation has failed to keep up with population growth and urbanization (Luoma and Rainbow 2008; Reza and Singh 2010). Numerous daily human activities, whether in the realm of the domestic, municipal, industrial, commercial, or agricultural, can release a range of metals into river water (Lester 1987; Gaillardet et al. 2003; Rose and Shea 2007; Luoma and Rainbow 2008). Metals such as As, Cd, and Pb in certain rivers of the region, especially in Thailand and Indonesia, have been found at levels exceeding WHO drinking water quality guidelines (Marcotullio 2007). From an environmental perspective, metal contamination within the river systems is the most complex of today's contamination issues. This is asserted because of the persistence of metals, compounded with their accumulative tendency in tissue, producing thereby food chain biomagnifications—with at base, of course, the toxicity of metals to living organisms (Adriano 2001; Luoma and Rainbow 2008). The determination of metal levels in river water is therefore considered a leading objective in environmental research (National Institute of Hydrology 1996–97).

Both bivariate and multivariate statistical analyses have been increasingly applied in environmental impact studies over the past two decades to reduce the complexity of datasets and thus lead ultimately to meaningful, logical data interpretation and conclusions. In the field of water management, these techniques have been used to assess the status of water quality and ecological systems, to investigate factors that are responsible for the temporal and spatial variations of metal concentrations in river water, and to identify potential sources of metal contamination (Schropp and Windom 1988; Schropp et al. 1990; Pekey et al. 2004; Singh et al. 2005; Alkarkhi et al. 2008; Krishna et al. 2009; Zhang et al. 2009; Jan et al. 2010; Li and Zhang 2010a; Li and Zhang 2010b; Sundaray 2010; Shin et al. 2013).

Concentrations of metals are not the only means of obtaining useful information on sources of contamination; stable isotopes of metals such Pb, Cr, Cu, Cd, and Hg can also be used to identify the source and fate of a contaminant. Recently, the determination of stable isotopes of metals has provided a potent new tool for successfully identifying and controlling emissions of metals, especially when conventional source tracking techniques cannot be employed (Diefenbacher 2009).

The present study was carried out as a preliminary study on metal pollution in four selected Southeast Asian rivers: 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 (Vietnam). The objectives of the study were to (1) determine the concentrations of metals in selected rivers of the SEA region, (2) distinguish the natural from the enriched metal concentrations in river water using a normalization technique, (3) identify the probable sources contributing metals into the rivers by using a multivariate statistical approach, and (4) apply the stable isotope signatures of Pb as a tracer of anthropogenic contamination.

Materials and methods

Study areas

With the objective of exploring the effects of urbanization and industrialization on metal concentrations in river water, water samples were collected from the four selected rivers (the Tonle Sap–Bassac, the Citarum, the lower Chao Phraya, and the Saigon) flowing through four main urban centers of the SEA region. The selection of these four was based on the presence of each in an extensive urban expansion area, and on the crucial role of each in its city's development. Their areas differ, however, in terms of demographics, economics, and environmental dynamics; these are summarized in Table 1.

Sample collection, preparation and analyses

Two river water sampling campaigns were conducted in 2010 to collect representative samples in both dry and wet seasons (Table S1 in the ESM). All sampling points along the river's course from the upstream to the downstream through each city were selected to represent the whole urban area (Fig. 1 and Fig. S1 in the ESM). In both sampling campaigns (dry and wet seasons), water samples were collected from the same location of each discrete point of sampling at a depth of 30 cm below the water surface. At each sampling location, a composite sample was obtained from a grab sample of river water collected from the middle of the river and also from both shorelines. Once a composite sample was obtained, a 0.45-μm pore size membrane filtration unit was used to collect the filtrated water into a pre-cleaned polypropylene bottle. Immediately after collection, all samples were acidified with concentrated HNO_3 to pH <2, stored at 4 °C, and then delivered to the laboratory for metal concentration analyses. During each water sample collection, on-site measurement of the usual water quality parameters, including temperature, pH, conductivity, and total dissolved solids (TDS) were also conducted using a Horiba D-54 hand-held water quality meter (Table S2 in the ESM).

For each sample collection trip, one set, consisting of a field blank sample and a trip blank sample, was also collected to ensure the quality of sample collection. All sample bottles

Table 1 State of geographic, demographic, economic, and environmental dynamics of the areas studied

| Information	Area studied			
	Phnom Penh, Cambodia	Bandung, Indonesia	Bangkok, Thailand	Ho Chi Minh City, Vietnam
Geographic information				
General description	The capital and largest city of the country	The capital of West Java province, the country's third largest city, and second largest metropolitan area	The capital and largest urban area of the country	The largest city in the country
Location	11°33′N 104°55′E	6°54′S 107°36′E	13°45′N 100°29′E	10°46′N 106°10′E
Total area (km^2)	375.00	167.67	1,568.74	2,095.01
Demographic information				
Total population (persons) (census year)	1,327,615 (2008)	2,393,633 (2010)	9,100,000 (2010)	7,162,864 (2009)
Population density(/km^2)	1,752	14,276	5,801	3,419
Economic dimension				
City GDP (billion US$)	NA	21	119	58
Environmental information				
Main river running through the city	Tonle Sap, Bassac, and Mekong Rivers	Citarum River	Chao Phraya River	Saigon River
Amount of wastewater treated (%)	0	23.4	42	<1

Hawksorth et al. (2009), http://www.apn-seawed.com/, accessed 30 Jan 2010, Marcotullio (2007), BMA (2007)

NA data is not available

were previously soaked in 10 % (*v/v*) HNO$_3$ overnight and afterwards rinsed with deionized water. All new 0.45-µm pore size membrane filtration units (Whatman Puradisc nylon syringe filters, 25 mm) were used.

Fig. 1 Maps showing sampling site locations along the Tonle Sap–Bassac Rivers. Note: Maps showing sampling locations for the Citarum River, lower Chao Phraya River, and Saigon River can be found in Fig. S1 in the ESM
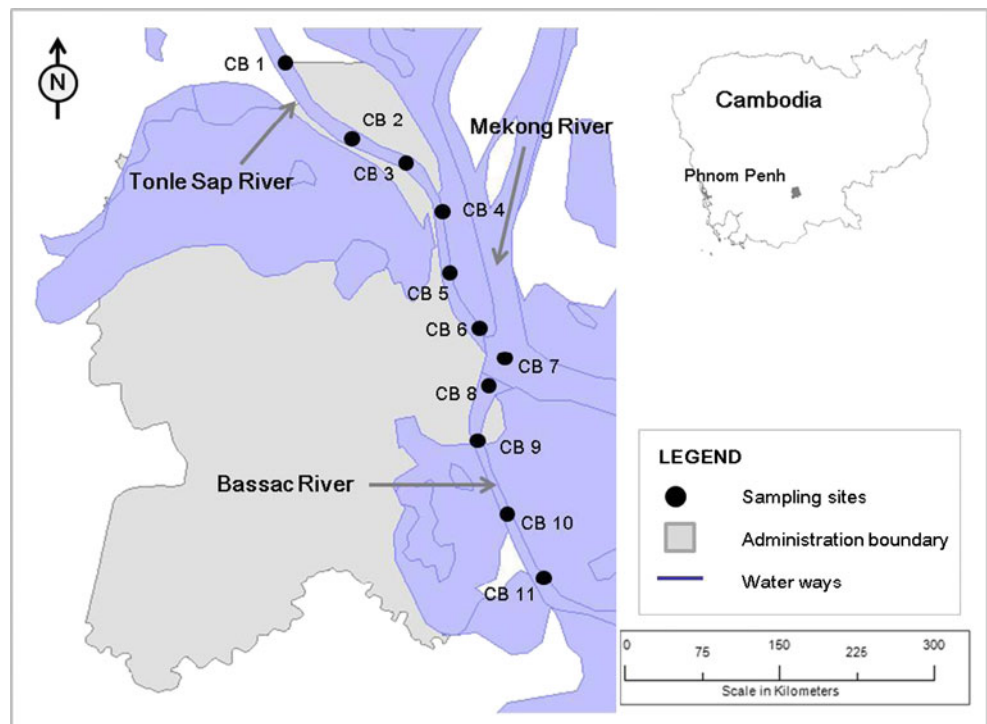
Following the standard methodology for the examination of water and wastewater (APHA-AWWA-WEF 1998), a well-mixed filtrated sample was analyzed directly for dissolved metal concentrations. The concentrations of 19 elements were determined by inductively coupled plasma mass spectroscopy (ICP-MS; Agilent 7500ce) and inductively coupled plasma optical emission spectroscopy (ICP-OES; Perkin Elmer Optical 5300DV). The target elements and their detection limits (in $\mu g\ L^{-1}$) were 0.03 Be, 0.33 Al, 0.08 Ti, 0.01 V, 0.01 Cr, 0.06 Mn, 0.63 Fe, 0.01 Co, 0.02 Ni, 0.08 Cu, 0.48 Zn, 0.04 As, 0.02 Se, 0.02 Mo, 0.02 Ag, 0.008 Cd, 0.04 Ba, 0.001 Tl, and 0.01 Pb.

For the solvent to use in solution preparation, and analytical procedures, 2 % (percent by volume) HNO_3 was prepared from 18.2 $M\Omega\ cm^{-1}$ deionized water obtained from a Millipore Milli-Q water purification system. The possibility of trace metal contamination in the 2 % HNO_3 was also checked and reported as an analytical blank (Table S3 in the ESM). Working standard solutions were prepared in a proper range of ICP-MS (0, 0.1, 1, 5, 10, 20, 50, 100 $\mu g\ L^{-1}$) and ICP-OES (0, 0.02, 0.05, 0.07, 0.1, 0.5, 1, 2.5, 5 $mg\ L^{-1}$) by suitable serial dilutions of Agilent multi-element stock solution (Agilent, Santa Clara, CA, USA) in 2 % HNO_3. The initial concentrations of ICP-MS and ICP-OES stock solutions were 10 and 100 $mg\ L^{-1}$, respectively. A correlation coefficient (r) of linear regression (concentrations of working standard solutions versus measured concentrations by ICP) of ≥0.998 was used for standard calibration curves.

Quality control and quality assurance for all instrumental analyses were conducted for each batch of 10 samples using an analytical blank sample (2 % HNO_3), an external standard (a particular standard concentration prepared from a stock solution obtained from Agilent), and a standard reference material (SRM 1643e: trace elements in water, obtained from the National Institute of Standards and Technology-NIST, MD, USA). The results of quality assurance (QA) and quality control (QC) during sample collection and sample analysis have been summarized in Table S3 in the ESM. In brief, no contamination by metals caused by the sampling procedure or sampling tools, or by the delivery procedure of samples could be detected; all metal concentrations in both field blanks and trip blanks were lower than the detection limits of ICP analytical methods. The recovery percentages for external standards and SRM were within 10 % of all certified values. The percentage differences of duplicate analysis were also within 10 % of all target elements.

Mass spectrometric isotope ratio measurement of three lead isotopes, ^{206}Pb, ^{207}Pb, and ^{208}Pb, occurring in the water samples was also conducted using the ICP-MS (Agilent 7500ce) following the method recommended by Watters et al. (1997). For this, SRM 981: common lead isotopic standard

reference material (obtained from NIST, USA) was used to prepare isotopic standards. A piece of SRM 981 wire (about 100 mg) was dissolved directly in a tared flask using 10 mL of 3 M HNO_3 in water, and heated on a hot plate. The acid concentration was then adjusted to 0.5 M HNO_3 and the final concentration of Pb in solution to 400 to 500 $\mu g\ g^{-1}$. Finally, this primary assay standard was further diluted for ICP-MS measurement to achieve a count rate of about 300,000 counts per second. For sample preparation of the isotope analysis, the water sample was weighed and mixed with the spike solution at the proportion of 1:1 in a clean conical tube. About 200 g of the spike calibration sample (CaI_3) was also prepared and run repeatedly to normalize any drift in instrumental mass bias. Analytical blanks of the same purified water and acid were prepared to assess any contamination occurring in the chemical and instrumental processing. The results of QA/QC indicated a ratio measurement of relative standard deviation of 0.2 % and no cross contamination.

Data analyses

An SPSS 15.0 for Windows software package was used to perform all statistical analyses on the database, including maximums and minimums, means, medians, standard errors, normality, seasonal variation in concentration, linear regression, and cluster analysis. Prior to the statistical analyses, all data sets were checked for normality of distribution by the Shapiro–Wilk test. Data for few of the parameters could be fitted to a normal distribution with 95 % confidence. Therefore, the Mann–Whitney U Test was performed to determine whether there was a significant seasonal difference in metal concentrations in the river water.

Normalization technique

In the present study, a normalization technique introduced by Schropp and Windom (1988) and Schropp et al. (1990) was applied to the database of metal concentrations to evaluate the contamination by metals in the river water. This method was based on statistical analyses of data on metal concentrations in the world's natural river systems obtained from the literature. Briefly, the statistical relationships between the concentrations of metals of interest and the concentrations of conservative elements were analyzed from the data on metal concentrations in the world's natural river systems. Then, a simple linear regression line and the upper and lower 95 % prediction limits were superimposed on our data of determined metal concentrations in the four SEA rivers. The river water was then judged as to whether there was metal contamination, according to where the points lay relative to the regression line and the prediction limits. All points which are found within the 95 % confidence bands of

the prediction limits can be characterized as containing metals that originated from the natural river system. On the other hand, if a point falls above the upper prediction limit, the river water is then considered to be contaminated by a particular metal. A greater distance above the prediction limit indicates a greater degree of contamination (Schropp and Windom 1988; Sakan et al. 2010). Both Al and Fe concentrations have been used successfully to normalize metal concentrations in order to indicate contamination by metals in the environment because they are among the most abundant crustal elements, and the ratios of metal concentrations to either Al or Fe concentrations are relatively constant (Schropp and Windom 1988; Schropp et al. 1990; Summers et al. 1996).

Cluster statistical analysis

Cluster analysis (CA) is a group of multivariate techniques serving as a straightforward method of congregating all cases, based on the characteristics they possess, into smaller groups or clusters of similarities within a cluster, and dissimilarities between different clusters (Singh et al. 2004; Singh et al. 2005, Shrestha and Kazaman 2007). The resulting clusters of cases should then exhibit high internal (within-cluster) homogeneity and high external (between cluster) heterogeneity. Hierarchical agglomerative clustering is the most common approach that provides intuitive similarity relationships between any case and entire data sets; typically these are illustrated by a dendogram (McKenna 2003, Shrestha and Kazaman 2007). The dendogram provides a visual summary of the clustering processes, presenting a picture of the groups and their proximity, with a dramatic reduction in dimensionality of the original data. The squared Euclidean distance usually gives the similarity between two samples and a distance can be represented by the difference between analytical values from the samples (Shrestha and Kazaman 2007).

To perform the hierarchical agglomerative CA in this study, the experimental data were first log-transformed. Log transformation results in data that are more constant in variance. The hierarchical agglomerative CA also standardized the data. Each variable (the experimental data) was standardized through z scale transformation (Singh et al. 2004; 2005; Ryberg 2006). Finally, clusters were successively merged on the basis of similarity of measurement and a linkage method. The linkage used to merge clusters was Ward's method. As summarized by Ryberg (2006), Ward's method uses an analysis of variance approach to evaluate differences between clusters. The two clusters that are merged are the pair that leads to the smallest increase in the sum of the within-group sums of squares. The within-group sum of squares is the sum of the squared Euclidean distances from each sample to the center of its parent group.

Stable lead isotopes determination

To assess the utility of dissolved lead as a tracer for different sources of lead contamination, the concentrations of three lead isotopes, ^{206}Pb, ^{207}Pb, and ^{208}Pb, in the water samples were compared to isotope compositions of various input sources as well as natural background lead levels obtained from the literature. Sources of lead contamination could then be identified using graphical methods (scatter plots) (Le Bot et al. 2011).

Results and Discussion

Concentrations of metals in river water and their seasonal variation

As a fundamental principle, knowledge of the natural background concentrations of the metals in river water is needed to assess the degree of metal contamination. While surveys of dissolved metal concentrations in natural waters have been going on since the 1970s (Luoma and Rainbow 2008), rivers in Asia have received relatively little attention (Gaillardet et al. 2003). Therefore, world average dissolved metal concentrations were used in the present study to assess the degree of metal contamination, since the natural background dissolved concentrations are not especially different among river systems (Luoma and Rainbow 2008). The research of Sindren et al. (2007) led to the conclusion that anthropogenic enrichment of metals in a river system could be revealed by metal concentrations exceeding the range of background concentrations.

In Cambodia, a comparison of dissolved metal concentrations in the Tonle Sap–Bassac Rivers with the average dissolved metal concentrations of world natural river systems (as background concentrations, from Gaillardet et al. 2003; Rauch and Pacyna 2001) found that two metals, V and As, were respectively about 1.2 and 2.5 times higher than their background concentrations (Table 2 and Tables S4, S5 in the ESM). High concentrations of V and As appeared along the water course at all sampling sites in both dry and wet seasons. Dissolved V and As concentrations in the dry season were respectively about 1.0 to 1.6 times and 2.5 to 4.4 times higher than those same metal concentrations in the wet season. The other dissolved metal concentrations were found to be lower than their background concentrations and present only at trace levels (concentrations<0.1 %).

In Indonesia, as Table 2 and Tables S4, S6 in the ESM reveal, dissolved concentrations of almost all metals (Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Ba, and Pb) in the Citarum River were higher than their background concentrations (Gaillardet et al. 2003; Rauch and Pacyna 2001), with average multiples of background concentrations of 3.0 (Al), 5.6 (Ti), 5.4 (V), 5.7 (Mn), 2.9 (Fe), 3.1 (Co), 1.8 (Ni), 1.5 (Cu), 16.7

Table 2 Comparison of average and median dissolved metal concentrations (in µg L^{-1}) of particular metals in four Southeast Asian rivers in Cambodia, Indonesia, Thailand, and Vietnam to the world average dissolved metal concentrations (in µg L^{-1})

	Al	Ti	Mn	Fe	Co	Ni	Zn	Cd	Pb
World average concentration	32.0 (n=42)	0.5 (n=27)	34.0 (n=37)	66.0 (n=38)	0.2 (n=30)	0.8 (n=29)	0.6 (n=33)	0.1 (n=14)	0.1 (n=20)
SD	179.0	1.2	12.5	185.9	0.1	2.2	4.6	0.1	0.9
Tonle Sap–Bassac Rivers, Indonesia									
Average	11	1	1	10	1	1	–	–	1
Median	8	1	1	11	1	1	–	–	1
SE	2.2	0.1	0.2	1.6	0.1	0.1	–	–	0.1
Citarum River, Indonesia									
Average	130	4	260	230	1	3	12	1	1
Median	100	3	195	195	1	2	10	1	1
SE	6.2	0.7	55.8	34.8	0.1	0.6	2.3	0.1	0.1
The lower Chao Phraya River, Thailand									
Average	100	1	210	100	1	8	53	1	1
Median	62	1	40	105	1	7	53	1	1
SE	7.7	0.1	110.5	34.2	0.2	0.5	3.9	0.1	0.1
Saigon River, Vietnam									
Average	245	2	90	370	1	2	75	40	2
Median	70	2	75	260	1	2	50	1	2
SE	134.8	0.4	11.4	142.4	0.1	0.3	19.4	81.2	0.4

All other dissolved metal concentrations are shown in the Electronic Supplementary Material (ESM)

SD is standard deviation; *SE* is standard error

(Zn), 3.6 (As), 1.6 (Mo), 1.4 (Ba), and 5.5 (Pb). The results of dissolved metal concentrations clearly indicate metal enrichment in the Citarum River system. Only dissolved Cr and Cd were present in lower than background value concentrations.

In the case of Bangkok, Thailand's lower Chao Phraya River, the multiples of dissolved concentrations times their background concentrations for Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Ba, and Pb were approximately 1.9 (Al), 3.5 (V), 1.4 (Cr), 1.1 (Mn), 1.6 (Fe), 3.6 (Co), 2.8 (Cu), 87.8 (Zn), 5.7 (As), 4.1 (Mo), 2.5 (Cd), 8.8 (Ba), and 6.8 (Pb) (Table 2 and Tables S4, S7 in the ESM). Generally, dissolved concentrations of the metals listed above were found to be 1–2 times higher in the dry season than in the wet. Only dissolved concentrations of Mn, Cu, and Pb were higher in the water samples collected in the wet season than in the dry. Ti was the only element with dissolved concentration lower than their background value.

In Vietnam's Saigon River, all dissolved metal concentrations except Ba were higher than their elemental background concentrations in undisturbed river systems (Table 2 and Tables S4, S8 in the ESM). Dissolved Zn concentrations were significantly higher (about 83 times) than the background value. Dissolved Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Mo, Cd, and Pb in the Saigon River had multiples of

about 2.2 (Al), 2.5 (Ti), 2.2 (V), 1.3 (Cr), 2.1 (Mn), 3.9 (Fe), 3.3 (Co), 2.8 (Ni), 2.2 (Cu), 1.1 (As), 1.2 (Mo), 10.9 (Cd), and 7.1 (Pb) times higher than their background values.

Overall, the results for dissolved metal concentrations in river water in the present study agree well with Elbaz-Poulichet et al. (1996), who found a greater anthropogenic imprint of dissolved metal concentrations by a factor of 2 to 4 times the unpolluted levels. As Luoma and Rainbow (2008) point out, metals that are relatively abundant in the Earth's crust change least in response to human inputs. Concentrations of elements that are relatively rare in the Earth, such as Cd, Ni, Cu, Zn, and Pb, are more greatly influenced.

Seasonal variation in metal concentrations

For Cambodia's Tonle Sap–Bassac Rivers, the Mann–Whitney *U* test results revealed a significant seasonal difference in the dissolved metal concentrations of Cr, Mn, Fe, Co, As, Se, Ba, and Pb ($p \leq 0.05$). The dissolved concentrations of Cr, Mn, and Fe were significantly higher in the wet season than in the dry, while As, Se, Ba, and Pb were significantly higher in the dry season than in the wet. Luoma and Rainbow (2008) concluded that even though dissolved concentrations are not

especially different among river systems, they can be variable over time within a river.

The results found here are however at variance with certain results reported by Gaillardet et al. (2003) and Luoma and Rainbow (2008), which indicated Fe and As were similarly dependent on pH, both decreasing in concentration with rising water pH. This difference in results may be attributed to such factors as the degree of abundance of the elements in the continental crust and their mobility during the weathering and transport process. This shows the need for more research into the processes that control the distribution of elements in Tonle Sap–Bassac river waters.

For Indonesia's Citarum River, the statistical analysis showed significantly higher Ti, Zn, and Ag concentrations in the wet season than in the dry ($p \leq 0.05$), while Mn and Co were found to be significantly higher in the dry season than in the wet ($p \leq 0.05$). Since Ti is a major element in rock and one of the most immobile elements in the Earth's surface (Gaillardet et al. 2003), high wet season Ti concentrations (about two times higher than in the dry season) may be due to strong erosion of the river bank. The moderately mobile elements Mn, Co, and V showed different characteristics of distribution from their chemical mobility during erosion. Cobalt (Co), in particular, tends to show decreasing concentrations with increasing pH. However, in this study, it was found that its concentrations were higher when pH was higher. This implies the presence of other parameters that control the concentrations of dissolved trace metals in the Citarum River.

In Thailand's lower Chao Phraya, the statistical analysis revealed significantly higher dissolved V and Mo concentrations in the dry season than the wet ($p \leq 0.05$). Concentrations of Cr, Fe, and Cu were significantly higher in the wet season than the dry ($p \leq 0.05$). The abundance of Cu and Cr in the wet season is in accordance with their chemical mobility, as noted in Gaillardet et al. (2003). The classification of trace element mobility in river water categorizes Cr and Cu as moderately mobile elements, with their mobility 10 to 100 times less than that of Na. Cu, moreover, forms strong complexes with organic matter (Elbaz-Poulichet et al. 1996).

In Vietnam's Saigon River, the statistical analysis showed non-significant differences ($p > 0.05$) in dissolved metals between the wet and dry seasons, except in Cu concentrations. The results indicate that the dilution effect usually observed in rivers in the wet season is not applicable to the Saigon River. The important conclusions from Bird (1987) on hydrological factors determining current spatial and temporal patterns of contamination are that the dilution effect in water quality depends on antecedent river flow conditions and river water pH, and that the prevailing dilution processes can occur at any time.

Rainwater's impact on the concentrations of elements, however, cannot be considered merely as simple dilution, because each water parameter follows its own evolution and characteristics (Santarsiero et al. 1996). For the Saigon River,

this limited dilution effect might be caused by the short period of Vietnam's rainfall and the flow recharge from the Saigon River to the various aquifers in Ho Chi Minh City.

Determination of the state of metal contamination in river water by a normalization technique

The interpretation of environmental metals data is made difficult by the fact that absolute metals concentrations in aquatic environments are influenced by a variety of factors, including both natural factors and anthropogenic enrichment. Thus, Schropp and Windom (1988) suggested that the determination of natural versus unnatural concentrations of metals and the determination of potentially available metals in the water column were the major aspects of understanding metal pollution. In order to address both of these aspects, a tool for interpreting metal concentrations (contamination) based on the relationships between naturally occurring metals and a reference element was employed.

In this present study, the ratios of dissolved trace metal concentrations to dissolved Fe concentrations were used because of the metals' relatively higher concentrations to Fe, compared to Al. Moreover, the resulting linear correlation coefficients of trace metal concentrations to Fe concentrations were higher than the correlation coefficients of those same trace metal concentrations to Al concentrations. The dissolved concentrations were the target of interest because dissolved metal concentrations are not only associated with natural processes (such as rock weathering) but also with other anthropogenic contributions (such as the use of metals in human activities) (Gaillardet et al. 2003).

With the exclusion of Ag, Be, and Ti, whose sparse concentrations were not suitable for the normalization technique, 8 of 15 metals in river waters from natural river systems exhibited a significant linear correlation with Fe (Table 3 and Table S9 in the ESM). The other seven trace elements, As, Ba, Cr, Cu, Mo, Se, and V, were not correlated with Fe. Therefore, they were excluded from further analysis.

To distinguish metal contamination (enrichment) from metals present under natural conditions by the application of regression relationships, results of the analyses of dissolved metal concentrations in these urban SEA rivers were plotted along with the regression lines and upper and lower 95 % prediction limits from data sets of dissolved metals in the natural river systems. Data for each of eight trace metals for which a significant linear relationship was noted are plotted versus Fe in Fig. 2a–h. All eight metals, Al, Cd, Co, Mn, Ni, Pb, Ti, and Zn, displayed concentrations elevated above their natural conditions levels, as Fig. 2 shows. Ti was the only trace element whose ratio to Fe indicated an origin from natural sources. The points of the remaining trace elements (Al, Cd, Co, Mn, Ni, Pb, Ti, and Zn) are located above the prediction limits. Notably, for Co and Zn, almost all locations

Table 3 Significant linear correlation coefficients ($p<0.05$) for metals and iron, according to the relationship: $\log(\text{metal}_{\mu g/L})=a+[\log(\text{Fe}_{\mu g/L})]$

Metal	n	r	Slope	Intercept
Aluminum	38	0.58	1.00	−0.55
Cadmium	17	0.55	0.86	−3.39
Cobalt	27	0.60	0.57	−2.26
Manganese	35	0.34	0.52	−0.34
Nickel	30	0.19	0.35	−0.71
Lead	21	0.47	0.79	−2.55
Titanium	27	0.38	1.33	−3.44
Zinc	32	0.39	0.50	−0.84

All correlations both significant and non-significant of metals to iron are shown in the Electronic Supplementary Material (ESM)

Fig. 2 Logarithmic scaling of **a** aluminum (Al), **b** cadmium (Cd), **c** ▶ cobalt (Co), **d** manganese (Mn), **e** nickel (Ni), **f** lead (Pb), **g** titanium (Ti), and **h** zinc (Zn) concentrations plotted against concentrations of iron (Fe). Linear regression lines and ±95 % prediction limits from the undisturbed river waters are superimposed on the data

sampled in all study areas showed serious contamination. Sakan et al. (2010) concluded that a greater distance above the prediction limit indicates a greater degree of enrichment caused by anthropogenic activities. Interestingly, Cd showed high enrichment in the river water collected from Vietnam. This display of Cd contamination agrees well with the results of dissolved metal concentrations of Cd in the Saigon River discussed above in Table 2 and Table S8 in the ESM. The highest and median dissolved Cd concentrations were about 245 and 1 µg L^{-1}, respectively. The source of elevated Cd concentrations in the Saigon River is suspected to be anthropogenic, a suspicion evinced by the significantly higher concentrations of Cd in the dry season than in the wet: the high Cd concentrations were therefore not being delivered to the river by drainage and runoff. Enrichment by Mn, on the other hand, was found in most sampling sites in Indonesia, Vietnam, and Thailand. As shown in Fig. 2, some points were below the lower prediction limit. In this case, analytical errors should be suspected and examined for Schropp and Windom (1988).

Cluster analysis and sources of metal contamination in river water

The Tonle Sap–Bassac Rivers, Cambodia

Cluster analyses were performed on the metals concentration data for each river in order to group together the sampling sites on that river having similar patterns of concentrations among the metals. These relations among sampling sites are visually represented in Fig. 3a–d by the length of the branches connecting them on a hierarchical dendogram for that river. The relationship among the Cambodian sampling sites is shown in Fig. 3a, in which four main clusters were identified from the cluster analysis.

A total of six sampling sites form cluster 1; they are considered the "extreme contamination group" of the Tonle Sap–Bassac Rivers system (CB1, CB2, CB3, CB4, CB6, and

CB7). Compared to the other sampling sites, river water collected at these six sites was contaminated with higher concentrations of Mn, Cu, As, Al, Tl, and Se. The concentrations of these metals ranged from 1–3 µg L^{-1} for Mn and As, 1–2 µg L^{-1} for Cu, 6–23 µg L^{-1} for Al, and 5–9 µg L^{-1} for Ba. The six sampling sites in this cluster can be divided into two subclusters, 1a and 1b (Fig. 3a). The subcluster 1a includes CB3, CB4, and CB6 sampling sites. CB3 and CB4 are located along the middle stream of the Tonle Sap River. Several poor communities are established in these areas. Five sewage pipes were found discharging municipal wastewater that had been treated by natural treatment systems into the Tonle Sap River (near the areas of the sampling sites). The concentrations of trace metals found in the effluent of the thusly treated sewage water, collected from the sewage pipes before discharge into the Tonle Sap–Bassac system, were usually higher than those same metal concentrations in the river waters. The concentrations of trace metals found in the effluent of treated sewage water (collected at the same time as river water samples) were 1–2 µg L^{-1} for V, Cu, and As; 1 µg L^{-1} for Cr, Co, Ni, Mo, Ag, and Tl; 7–9 µg L^{-1} for Mn; 7–8 µg L^{-1} for Zn; 25–30 µg L^{-1} for Ba; and 160–255 µg L^{-1} for Al. Concentrations of Al and Mn were particularly high, 19.4 and 9.6 times higher than in the river waters. Discharge of sewage water is therefore likely to be the major contributor of trace metals to the Tonle Sap River. Two ferryboat landings located near to the CB3 site may also be contributing some amounts of metals into the rivers. The other subcluster, 1b, consists of the three sampling locations CB2, CB7, and CB1. As shown in Fig. 3, locations CB2 and CB7 are on the same branch of subcluster 1b, while site CB1 is alone on its branch of subcluster 1b. River waters collected from sampling sites CB2, CB7, and CB1 were found with higher concentrations of Mn (1–2 µg L^{-1}), Cu (1 µg L^{-1}), As (1–3 µg L^{-1}), and Al (14–23 µg L^{-1}) compared to the other sampling sites. Site CB1 is located in the most upstream of the section of the Tonle Sap that passes through Phnom Penh city. Several sand pumping stations are likely the main contributors of trace metals into the river at site CB1. These sand pumping stations usually discharge wastewater generated at the pumping stations into the river without proper treatment. The likely sources of metals entering into the river at location CB2 are poor communities inhabiting homes on the riverbank and floating houses in the river itself. Residents in this area (CB2) till gardens in the fertile riverbank soil using traditional practices. These methods, however, allow Al, one of the most abundant elements in the Earth's crust, to be delivered into the river by surface runoff. At site CB7, the sources of metals are
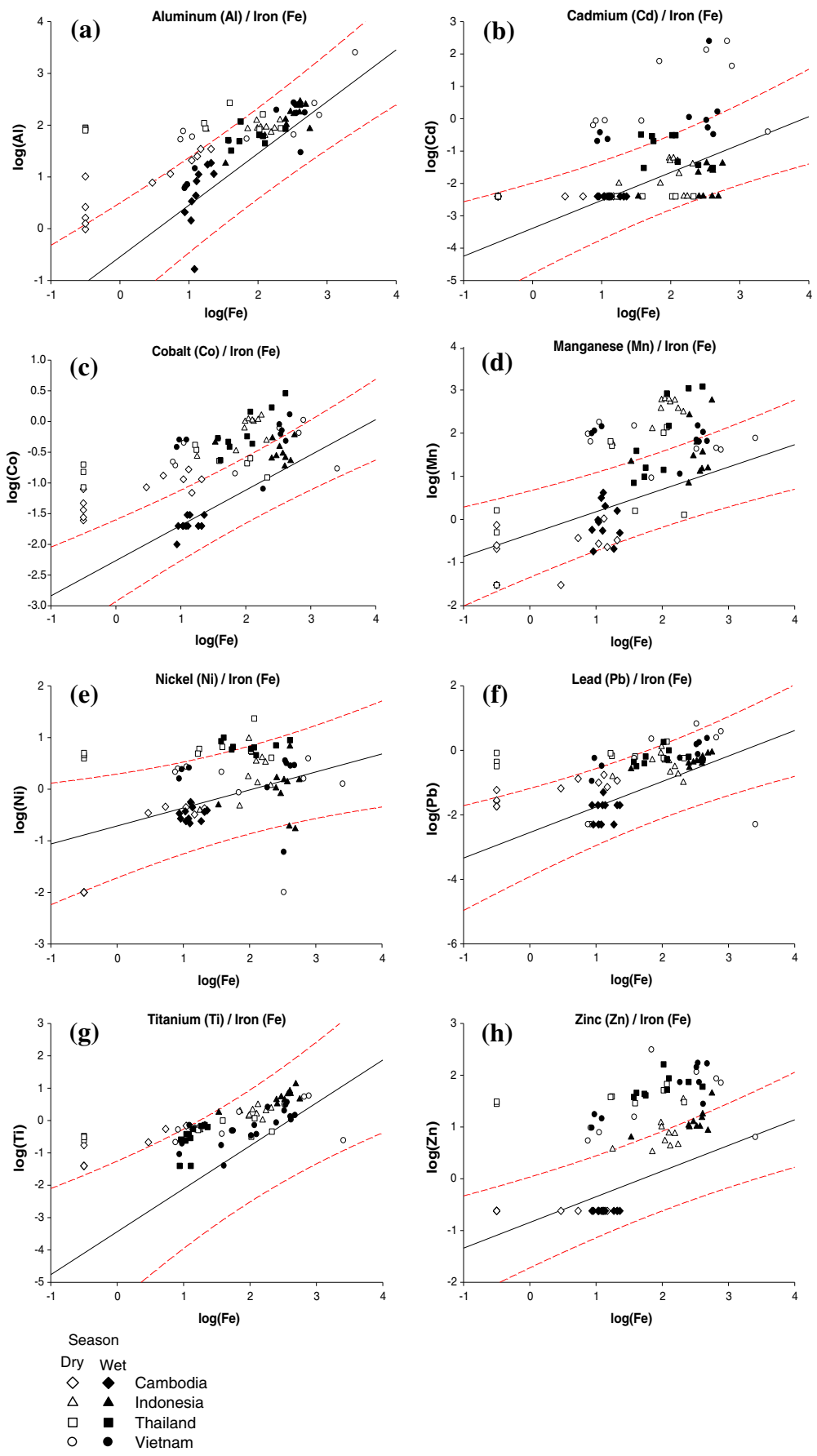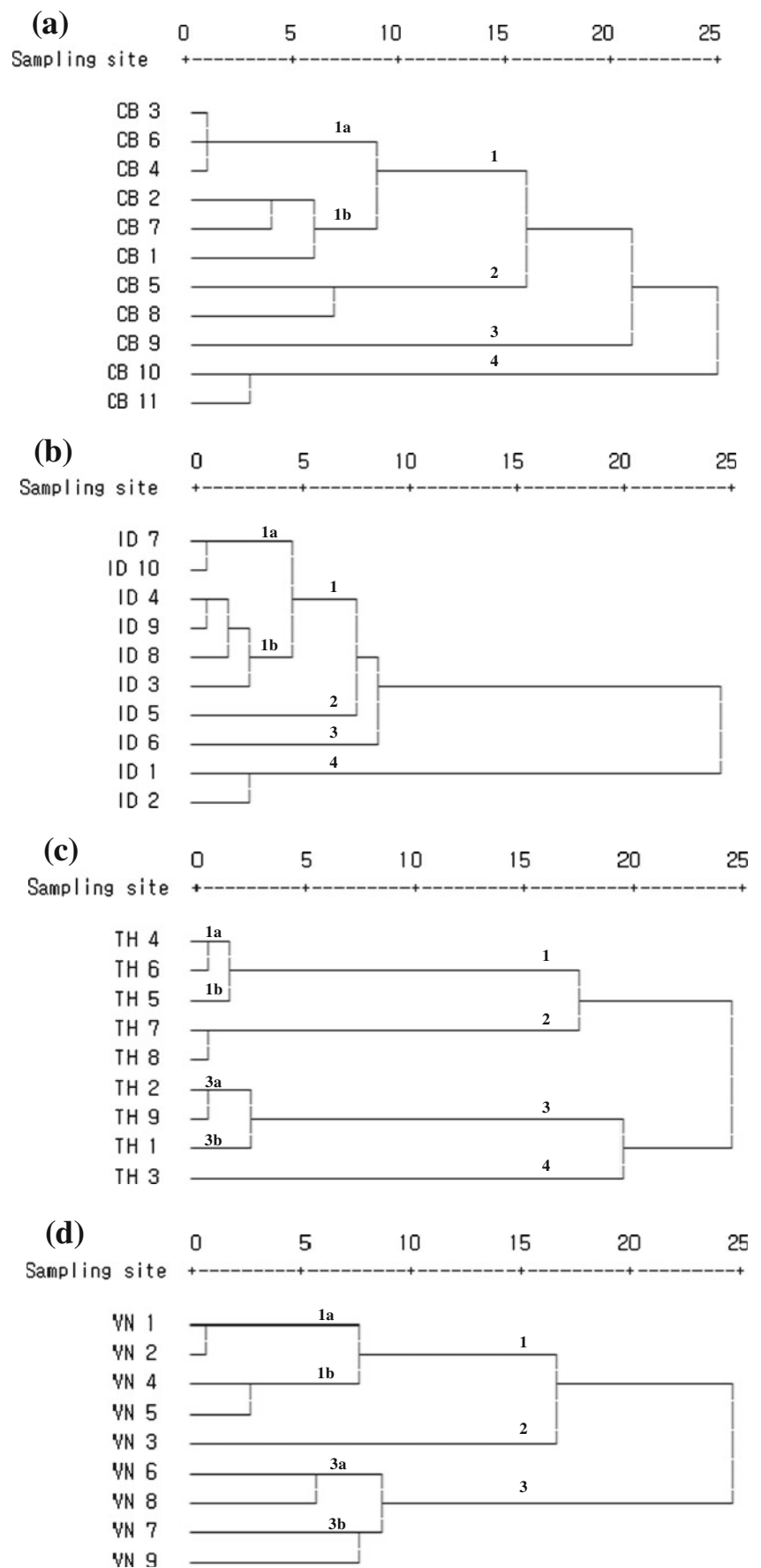
Season

Dry Wet

◇ ◆ Cambodia
△ ▲ Indonesia
□ ■ Thailand
○ ● Vietnam

Fig. 3 Dendogram showing clustering of sampling sites along **a** the Tonle Sap–Bassac Rivers, **b** the Citarum River, **c** the lower Chao Phraya River, and **d** the Saigon River

considered to be the Mekong River and sand pumping stations; this site is at the conjunction of the Tonle Sap River and Mekong River.

Cluster 2 can be called a "clean group" of the Tonle Sap–Bassac river system. There are two sampling locations (CB5 and CB8) included in this cluster. Locations CB5 and CB8 are located in the downstream of the Tonle Sap and at the mixing point of the Mekong River and Tonle Sap River. Human activity is at a lower level along the rivers in these two areas.

The third cluster can be also considered a "clean group" of this river system (CB9). Low concentrations of trace metals were determined in the river waters collected at this sampling site. Only elevated concentrations of Co were found, with an average concentration of 2 μg L^{-1}. The Co concentration found in this location was about 34.4 times higher than the average Co concentration in the entire length of the Tonle Sap–Bassac river system.

Two sampling sites (CB10 and CB11) are grouped into cluster 4, in the downstream of the Tonle Sap–Bassac system. Compared to other clusters, the river waters in this cluster can also be considered as clean, with concentrations of all metals lower than other sampling sites. Even though these two sampling sites are located in the most downstream of the Tonle Sap–Bassac system (and below Phnom Penh city), the metal concentrations were found to be lower than those in waters collected from the upstream and middle stream of the river system. This may be due to the lower level of human activity in these areas. Moreover, the contribution of water loading from the Mekong River may have a diluting effect on metal concentrations in this part of the system.

The Citarum River, Indonesia

As shown in Fig. 3b, the first cluster (cluster 1) categorized by the cluster analysis is considered a "heavily (extremely) contaminated group." There are five sampling stations (ID3, ID4, ID7, ID8, ID9, and ID10) included into this cluster. Very high concentrations for almost all trace metals (most showing their highest concentrations for this river) were found in the river water collected from these five locations. Concentrations of metals were 1 μg L^{-1} for Be, Co, Mo, and Pb, 1–2 μg L^{-1} for Cr, 1–5 μg L^{-1} for Ni, 2–5 μg L^{-1} for Ti, Cu, and As, 3–6 μg L^{-1} for V, 15–55 μg L^{-1} for Al, 95–210 μg L^{-1} for Al, and 205–345 μg L^{-1} for Mn. Sampling site ID3 is located in the upper stream of the Citarum River. Monitoring stations ID4 and ID7 are located in the middle stream, and sites ID8, ID9, and ID10 in the downstream of the river. Although site ID3 (in subcluster 1b) is located in the upper part of the river, high concentrations of all trace elements were found there. Concentrations at the other sites in the cluster, however, were even higher.

The upper stream of the Citarum is characterized by sporadic industrial sprawls, mostly textile industries. Another 1b subcluster, including sampling sites ID4, ID8, and ID9, had higher concentrations of all metals compared to site ID3. Lastly, subcluster 1a comprises two sampling sites located the most downstream on the Citarum, and covers an area called Bandung Metropolitan. The river waters of subcluster 1a were found to be extremely contaminated, with the highest concentrations of most metals. These two areas (ID7 and ID10) are the densest industrial and residential areas in the river basin. These areas combine high levels of industrial and residential activities with low-efficiency wastewater treatment systems. Therefore, the discharge of wastewater, mainly from industries and domiciles, is regarded as the source of metals in this cluster.

Sampling site ID5, constituting cluster 2, can be called a "moderately contaminated group." Still, high concentrations of several trace metals, including Mn (440 μg L^{-1}), Fe (385 μg L^{-1}), Ni (2 μg L^{-1}), Zn (40 μg L^{-1}), As (4 μg L^{-1}), Se (1 μg L^{-1}), and Ba (50 μg L^{-1}) were found. Concentrations of Al (105 μg L^{-1}), V (3 μg L^{-1}), Cr (1 μg L^{-1}), Ti (4 μg L^{-1}), Co (1 μg L^{-1}), and Cu (3 μg L^{-1}) can also be considered as at elevated levels. This sampling site (ID5) is located in the middle stream of the Citarum River, where there is also intense industrial activity with ineffective wastewater treatment systems.

Sampling site ID6 constitutes cluster 3, another "moderately contaminated group." The concentrations of several trace metals found in the samples taken from this site were lower than those same metals' concentrations in the river water samples collected from site ID5 in cluster 2. The different patterns of which metals showed high and low concentrations thus distinguish cluster 3 from 2. The highest concentrations in the Citarum of the metals Ni (5 μg L^{-1}), Cu (4 μg L^{-1}), As (4 μg L^{-1}), and Mo (1 μg L^{-1}) were found as well at ID6. The source of metal contamination in this area is considered to be the discharge of wastewater from intense industrial and residential activities.

The last cluster, cluster 4, consists of sampling sites ID1 and ID2, located in the upper part of the Citarum River. The samples here were relatively cleaner, with concentrations of all metals of interest lower than in samples from other sites.

The lower Chao Phraya River, Thailand

The relationship among the Thai sampling sites is shown in Fig. 3c, in which four main clusters were identified from the cluster analysis.

Cluster 1 can be labeled the "contaminated group" of the Chao Phraya River (TH4, TH5, and TH6). These three sampling sites are located in traditional low-income residential areas of Bangkok. The trace metals analysis of these river waters determined elevated concentrations of Cu, Zn, and Ba.

Their average concentrations varied from 1–5 µg L^{-1} for Cu, 28–45 µg L^{-1} for Zn, and 115–140 µg L^{-1} for Ba. This cluster can be further divided into two subclusters Fig. 3c. Subcluster 1a is formed by TH4 and TH6, which are in dense residential areas. The main land uses in these areas are the floating markets (TH4) and residential zones (TH6).

The second cluster can be termed an "extremely contaminated group" of the Chao Phraya system (TH7 and TH8). The river waters in this group were contaminated with high concentrations of Mn, Co, Ni, Fe, Zn, and Ba. The respective ranges of these six were 390–455 µg L^{-1}, 1 µg L^{-1}, 4–15 µg L^{-1}, 90–210 µg L^{-1}, 43–50 µg L^{-1}, and 50–170 µg L^{-1}. Both sampling sites in the cluster represent industrial and commercial zones of Bangkok. Sampling site TH7 is located in the suburban community around Suvanabhumi airport, and site TH8 in a new economic zone along the Chao Phraya River.

The third cluster can be considered the "clean group" of the Chao Phraya River system (TH1, TH2, and TH9). Generally low concentrations of trace metals were identified in the river waters collected from these three sampling sites. However, elevated levels of Cu, Fe, and Zn were detected. The concentrations of Cu, Fe, and Zn varied from 2–3 µg L^{-1}, 16–33 µg L^{-1}, and 22–30 µg L^{-1}, respectively. The sampling sites in this cluster can be divided into two subclusters Fig. 3c. Cluster 3a includes the river water samples collected from the middle stream (TH2) and the raw water for water supply production (TH9), while cluster 3b (TH1) represents the Chao Phraya River coming into Bangkok. TH1 is in the most upstream of the section of the river flowing through Bangkok.

There is only one sampling site, TH3, placed in cluster 4, in the downstream of the Chao Phraya River. Compared to other sampling sites, high concentrations of Ni (5.27 µg L^{-1}), Ag (0.22 µg L^{-1}), Tl (0.09 µg L^{-1}), and Se (0.23 µg L^{-1}) were found in the river waters collected from sampling site TH3.

The Saigon River, Vietnam

Figure 3d displays the hierarchical dendogram obtained by cluster analysis for the Saigon River. Four sampling sites (VN1, VN2, VN4, and VN5) are grouped into cluster 1. These four sampling sites can be divided into two subclusters, 1a (VN1 and VN2) and 1b (VN4 and VN5). Subcluster 1a can be called a "lightly contaminated group," though with higher Mo and Se concentrations than the other sampling sites. The average concentrations of both Mo and Se were about 1 µg L^{-1}. These two sampling sites are located in the downstream section of the Saigon River. Even though these areas, especially VN1, are heavily navigated, the concentrations of metals were generally lower compared to other areas. Subcluster 1b comprises sampling sites VN4 and VN5, located in the middle stream of the river. High concentrations of
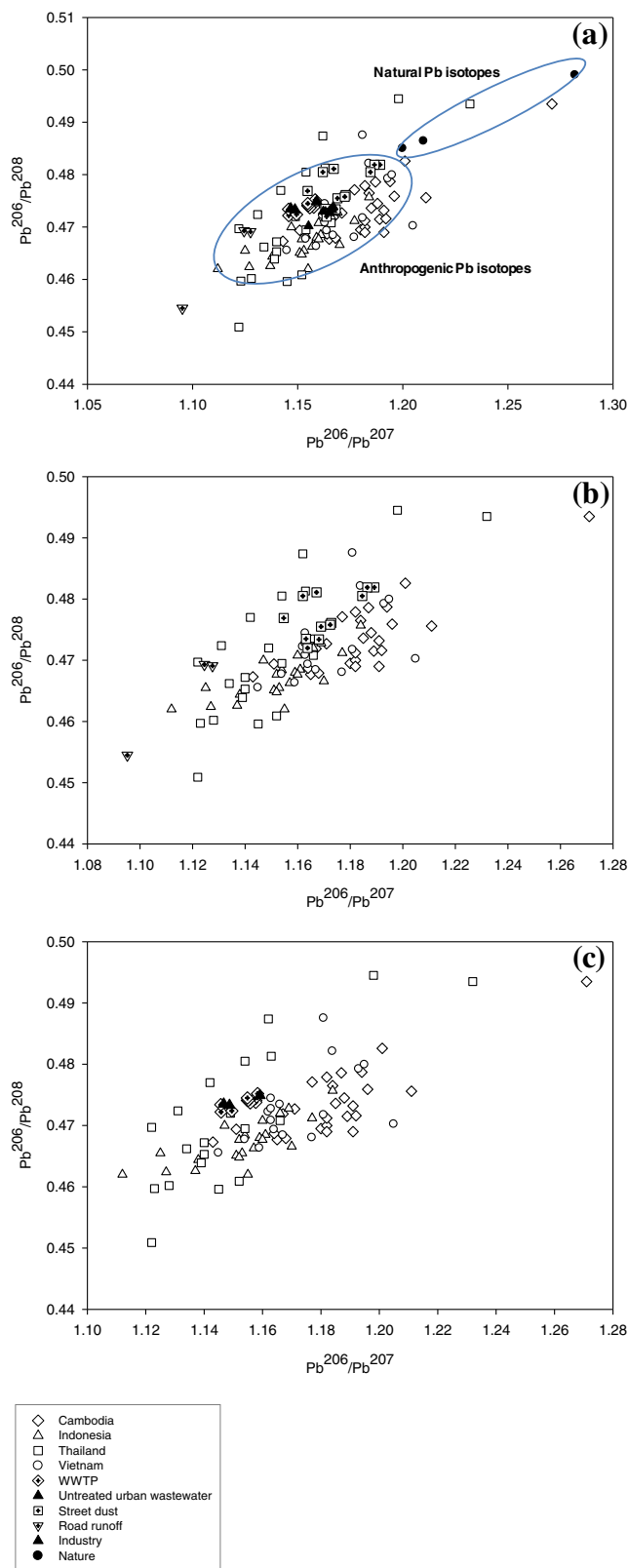

Fig. 4 ^{206}Pb/^{207}Pb ratio as a function of ^{206}Pb/^{208}Pb in urban river waters of Southeast Asian countries (Cambodia, Indonesia, Thailand, and Vietnam), in comparison with **a** several sources of Pb pollution, **b** urban wastewater, and **c** street dust and runoff, obtained from previous studies

Mn (150 μg L^{-1}) and Ba (23 μg L^{-1}) were found in these areas. Discharges of wastewater from industrial and human activities are regarded as the source of metals in these waters.

Cluster 2, consisting of sampling location VN3, can be considered a "lightly contaminated" site for most metals, except for Al and Fe. The highest concentrations of Al and Fe here were determined to be as great as 1,250 and 1,300 μg L^{-1}, respectively. Such high Al and Fe concentrations would indicate serious soil erosion in this area.

Four sampling sites (VN6, VN7, VN8, and VN9) are grouped into cluster 3 and can be divided into two subclusters. Sampling locations VN6 and VN8, the members of subcluster 3a, are located in the middle stream of the river, a stretch where soil erosion usually occurs. The erosion of soil and discharges of domestic and industrial wastewater are expected to have raised the concentrations of Ti (4–5 μg L^{-1}), Cr (2–6 μg L^{-1}), Ni (2–4 μg L^{-1}), Cu (6–10 μg L^{-1}), Cd (20–250 μg L^{-1}), Al (160–220 μg L^{-1}), and Fe (510–630 μg L^{-1}) in the river waters. Subcluster 3b consists of locations VN7 and VN9, which are in the upstream of the Saigon River. These upstream locations are areas with diverse and rapidly developing agricultural and aquaculture activities. They are therefore assumed to be the sources of the elevated Cr (1–3 μg L^{-1}), Zn (120–190 μg L^{-1}), Cd (30–70 μg L^{-1}), and Ba (10–26 μg L^{-1}) concentrations in the Saigon River.

Application of stable lead isotopes as a tracer of contamination sources in Southeast Asian rivers

Figure 4 shows a scatter plot of stable lead isotopes data (^{206}Pb/^{207}Pb and ^{206}Pb/^{208}Pb) which have been used widely for interpreting data in environmental studies (Oulhote et al. 2011). Comparisons of lead isotopic compositions of river water samples with those of various pollution sources and in the natural background (obtained from previous studies: Flegal et al. 1987; Monna et al. 1995; Bing-Quan et al. 2001; Gobeil et al. 2005; Harlavan et al. 2010) were plotted to identify the possible sources of lead contamination. In this study, the isotopic ratios of ^{206}Pb/^{207}Pb and ^{206}Pb/^{208}Pb, considered to represent natural Pb, were 1.20–1.28 and 0.48–0.50, respectively. Representing anthropogenic Pb were the isotopic ratios of ^{206}Pb/^{207}Pb at 1.12–1.19 and ^{206}Pb/^{208}Pb at 0.46–0.48.

The scatter plot (Fig. 4a–c) clearly reveals that anthropogenic sources are the major source of Pb contamination in the urban river water of SEA. Both point sources (wastewater treatment plants, power stations) (Fig. 4b) and non-point sources (atmospheric wet deposition, street runoff, street dust, automobile exhaust) (Fig. 4c) can be significant sources contributing Pb into river waters. Natural Pb contributions through sediment and seawater were found at some sampling sites in Thailand and Vietnam. The stable Pb isotopic ratios found in this study were distinct from those of the natural Pb components.

Conclusions

Water samples from rivers in Southeast Asian countries collected at a range of discrete points in time were found contaminated with several metals. Concentrations of most target metal elements exceeded background concentrations for those metals. The variability of metal concentrations was site- and time-specific. A normalization technique confirmed that concentrations of Al, Cd, Co, Mn, Ni, Pb, and Zn were enriched in the rivers by other than natural sources. The results of both cluster analysis and stable lead isotopes analyses indicate that anthropogenic sources, including non-point sources (road runoff and street dust) and point sources (discharges of both industrial and household wastewater) are the major contributors of metal pollution into these rivers. A continuous monitoring program of trace metals should therefore be conducted. Future research should focus on the collection of bed sediments to obtain a more time-integrated idea of metal contamination.

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