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Spatial variation and risk assessment of trace metals in water and sediment of the Mekong Delta



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h i g h l i g h t s

- Trace metal transportation are controlled by SPM concentrations.
- Dissolved trace metal distribution vary in the salinity gradient.
- Ecotoxicological indexes in surface sediments show low to medium contamination.

a r t i c l e i n f o

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The Mekong Delta, is home to 17 million inhabitants and faces numerous challenges relating to climate change, environmental degradation and water issues. In this study, we assess trace metals concentrations (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Hg, Pb) in the water, suspended particulate matter and surface sediments of the Tien River, the Northern branch of the Mekong Delta, during both dry and rainy seasons. Metal concentrations in the dissolved and suspended particle phases remain in the low concentration range of the main Asian Tropical River. During transportation in the riverine part, we evidenced that V, Cr, Co, As and Pb are dominant in the particulate phase while Mo, Ni and Cu dominate in the dissolved fraction. In the salinity gradient, dissolved U, V, Mo exhibit conservative behaviour while Ni, Cu, As, Co and Cd showed additive behaviour suggesting desorption processes. In the surface sediment, metal concentrations are controlled by the particle-size, POC contents and Fe, Al and Mn oxy(hydr)oxides. Calculated Enrichment Factor and Geoaccumulation Index evidenced As enrichment while the calculated mean effect range median quotients evidenced a low to medium ecotoxicological potential effects range in the surface sediments.

1. Introduction

Deltas and estuaries play a major role in material and element transport from river to ocean and on biogeochemical cycles. The various physical and chemical gradients that occur in this mixing environment affect the partitioning, mobility and reactivity of elements such as nutrients and trace metals (e.g. [Du Laing et al.,](#)

[2008; de Souza Machado et al., 2016; Garnier et al., 2010](#)).

Because of their persistence, toxicity and ability to accumulate in organisms, trace metals are major pollutants and are considered a high priority (i.e. European Water Framework Directive ([Anonymous, 2000](#)), US-EPA (40 CFR Part 423, Appendix A). Trace metals in aquatic environments originate mostly from natural erosion and soil leaching. They are also released by human activity such as industrial, domestic, urban and agricultural practices. Suspended particles are a key factor in contaminant transport from the continent to the ocean, making their quality assessment a major scientific concern (e.g. [Apitz and Power, 2002](#)). Understanding the processes controlling elemental transport and reactivity between

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the dissolved and particulate (both suspended and deposited sediments) phases in rivers and more particularly in estuaries is thus crucial to assess their impact in terms of contamination and ecotoxicological risks.

The Mekong River is the longest River in Southeast Asia with a total length of 4800 km and a drainage basin of 795,000 km². It originates in the Tibetan Plateau of western China and flows southward through China, Myanmar, Laos, Thailand, and Cambodia, before entering Vietnam through the Delta and then discharging into the South China Sea. The Mekong Delta is one of the world's largest deltas (39 000 km²) and has a population of around 17 million people (GSO, 2016). It is the principal area of rice production in Vietnam and its economy is largely reliant on agriculture (namely rice and fruit) and aquaculture (mainly shrimp and catfish). Despite recent intensification of agricultural and aquaculture activity as well as rapid urban growth, the Mekong Delta remains one of the poorest regions in Vietnam (Renaud and Künzer, 2012). The delta's natural and social systems face numerous challenges related to climate change, environmental degradation and water issues such as flooding, water pollution and access to water (Xue et al., 2011; Renaud and Künzer, 2012). Hydroelectric dams on the Mekong River and its tributaries have severely impacted the aquatic ecosystem's biodiversity (Campbell, 2012). Sediment supply to the delta and the ocean is also impacted, and estimates suggest that it retains about 32.41 million tons of sediment per year (Kummu et al., 2010). Indeed, before dam construction, the Mekong was one of the 10 largest sediment suppliers to the world's oceans with an annual sediment flux estimated at around 160 million tons (Milliman and Meade, 1983; Milliman and Ren, 1995). Numerous dams are currently under construction or in the planning stages on the main stream and in the tributaries, increasing the vulnerability of the Mekong River. The Mekong Delta river quality is also threatened by the development of intensive agricultural and aquaculture activity and the release of pesticides (Toan et al., 2013), antibiotics (Giang et al., 2015), nutrients and trace metals (Wilbers et al., 2014).

Information on trace metal risk assessment in the Mekong Delta's waters and surface sediments is not readily available (e.g. Cenci and Martin, 2004; Noh et al., 2013; Wilbers et al., 2014) and studies that are available have mainly focused on arsenic groundwater contamination issues and consequences to population health (Berg et al., 2007; Buschmann et al., 2008; Hoang et al., 2010). Thus, considering the environmental challenges that are facing the Mekong Delta, the purpose of this study is to evaluate trace element contamination (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Hg, Pb, U) of the Tien River, Mekong Delta, Vietnam. Two snapshot campaigns were performed along the Tien River during the contrasted seasons (dry and rainy seasons). The objectives were (i) to get an inventory of dissolved and particulate polymetallic concentrations which affect the quality of the river, (ii) to identify the fate of metal distribution in the water column and sediment and the factors controlling their partitioning, and (iii) to provide a risk assessment of surface sediments based on geochemical and ecotoxicological indexes.

2. Material and methods

2.1. The Tien River, Mekong Delta, Vietnam

The Mekong Delta begins in Phnom Penh, Cambodia, where the river divides into its two main branches, the Mekong and the Bassac, which are respectively subdivided into six and three branches, the Tien River being the northern branch of the Delta (Fig. 1, 150 km long, 450–2250 m width, up to 10 m depth). The Mekong Delta is composed of Holocene alluvial sediments of

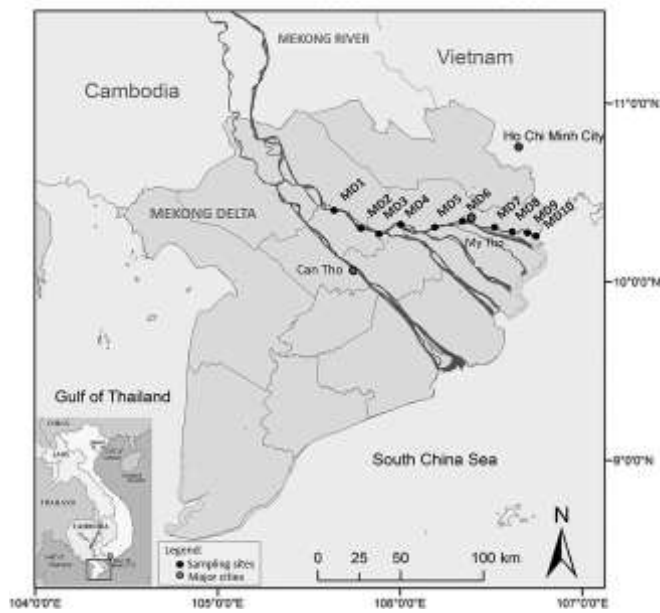


Fig. 1. Sampling location map.

marine and fluvial origin that were rapidly deposited beginning 8000 year BP (Nguyen et al., 2000; Xue et al., 2011). The climate is monsoonal humid and tropical, with average temperatures of 27–30 °C. The rainy season (approximately 80% of the annual rainfall) lasts from May to October. Accordingly, the Mekong River discharge reaches a minimum in April–May and a maximum in September–October in the lower Mekong (Xue et al., 2012) and the same is true for the Bassac River where the river discharge fluctuates from 200 m³ s⁻¹ to 7000 m³ s⁻¹ respectively (Loisel et al., 2014).

2.2. Sampling and handling

Two snapshot campaigns were conducted along the Tien River during dry and wet seasons, in March and October 2013, respectively. At each site (Table 1a), temperature, pH, dissolved oxygen, conductivity and salinity were immediately measured in situ using a multi parameter probe (WTW 3420®). Then, water was sampled at 10–50 cm below surface using a Niskin non-metallic water sampling bottle (General Oceanic®) and stored in 5L PE bottle. All filtered and unfiltered samples were stored in a cooler (~4 °C) until being brought back to the laboratory. A first filtration was performed on glass microfiber filter (0.7 μm GF/F Whatman®, pre-weighed and preheated at 500 °C). The filtrate was stored in a 60 ml bottle and kept at –18 °C for analyses of dissolved nutrient while filters, used for determination of suspended particulate matter (SPM) and particulate organic carbon (POC) concentrations, were dried at 50 °C, then weighed and stored at room temperature. A second filtration was realized on pre-weighed PTFE filters (0.20 μm Omnipore®) for analysis of particulate and dissolved trace metals. After filtration, the filtrate was acidified (Normapur HNO₃ 2% v/v) and stored in a 30 ml acid pre-cleaned PP bottle (Normapur HNO₃ 10% v/v) at 4 °C while the filters were kept in sterile plastic petri dishes at –18 °C, then freeze-dried, weighed and stored in the plastic petri dishes. To prevent contamination during collection and handling, all equipment was cleaned and we wrapped each sub-sample individually in two polyethylene bags. Surface sediments were collected at each site using a Shipek sediment grab sampler, immediately stored in PE bags at –18 °C and, freeze-dried.

Table 1a
Location of sampling site: GPS coordinates and main characteristics.

Sampling site	Coordinates	City	Activity	
MD-1	N10°24'51.000	E105°39'11.800	Cao Lanh City, 110 000 inhabitants	agriculture: rice, fruit; industrial activity
MD-2	N10°17'55.700	E105°46'06.400	Sa Dec City, 160 000 inhabitants	agriculture: fruit
MD-3	N10°16'38.300	E105°54'24.500	My Thuan City, 160 000 inhabitants	agriculture: fruit; industrial activity
MD-4	N10°19'09.200	E106°01'12.300	Cai Be City, 260 000 inhabitants	agriculture: fruit
MD-5	N10°18'57.000	E106°12'02.000	Rural area	agriculture: rice, fruit
MD-6	N10°20'53.400	E106°21'02.600	My Tho City, 230 000 inhabitants	agriculture: fruit; industrial activity
MD-7	N10°18'35.800	E106°30'17.900	Rural area	agriculture: rice, fruit; aquaculture: fish
MD-8	N10°17'11.600	E106°34'56.100	Rural area	agriculture: rice, fruit; aquaculture: shrimp
MD-9	N10°17'19.300	E106°41'39.000	Rural area	agriculture: rice, fruit; aquaculture: shrimp
MD-10	N10°15'36.800	E106°45'19.000	Rural area	agriculture: rice, fruit; aquaculture: shrimp

2.3. Laboratory analyses

2.3.1. Trace metal analyses

Particulate trace metals on PTFE filters (Metals_{SPM}) and representative sub-samples of surface sediments (Metals_{SED}; 100 mg of dried, powdered and homogenized material) were analyzed by a microwave total extractable acid digestion (NovaWave SCP Sciences®, IGE-OSUG Laboratory, Grenoble, France; HCl, HNO₃, HF; Trace Metal grade Fisher®). The protocol is based on the digestion method USEPA 3052 and is fully described in [Strady et al. \(2017\)](#). Trace metal concentrations (V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Pb, U) were measured by ICP-MS (Elan DRC II Perkin Elmer, TERA Environment Laboratory Fuveau France) while Al, Mn and Fe concentrations were measured by ICP-AES (Varian 720 ES, ISTERre-OSUG Laboratory, Grenoble, France) using external calibration for both cases. Total Hg concentrations in sediments IHg_{SED} were determined by atomic absorption spectrophotometry after dry mineralization and gold amalgamation by using an automatic mercury analyzer (Altec, Model AMA 254 ISTERre-OSUG Laboratory, Grenoble, France) ([Gue' dron et al., 2009](#); [Strady et al., 2017](#)). Metal concentrations were directly measured by ICP-MS (Elan DRC II Perkin Elmer) using external calibration. When the sample salinity was up to 1, dissolved trace metals were determined by Kinetic Energy Discrimination -Argon Gas Dilution (KED-AGD mode) with the Thermo Scientific iCAPQ ICP-MS (Plateforme AETE-HydroSciences/OSU OREME, Montpellier, France) using an added on-line internal solution (Sc, Ge, In and Bi) to correct signal drifts. The analytical quality assurance of particulate measurements was assured by analyzing certified reference materials. Accuracy was V: 6%; Cr: -6%; Co: 7%; Ni: -2%; Cu: -6%; Zn: 30%; As: 1%; Mo: -3%; Cd: -13%; Pb: -8%; Hg: 9% for GBW-07323 (n ¼ 5) and V: 1%; Cr: -6%; Co: -7%; Ni: -13%; Cu: -9%; Zn: 29%; As: -5%; Mo: -3%; Cd: 2%; Pb: -9%; Hg: 5% for MESS-3 (n ¼ 4). Precision was lower than 8% for all elements and both GBW-07323 and MESS-3.

2.3.2. Particulate organic carbon analyses

A combustion infrared detection technique using a LECOCS-125 analyzer (EPOC Laboratory, Talence, France) with 5% precision was used to determine POC concentrations. Contents of POC are expressed as a percentage of the dry weight of SPM or sediment, abbreviated as POC%.

2.3.3. Orthophosphates, nitrates and ammonium analyses

Orthophosphates (P-PO₄) were analyzed using the ascorbic acid-molybdate blue method developed by [Murphy and Riley \(1962\)](#) prior to spectrophotometric measurements. Ammonium (N-NH₄) was analyzed directly on site using the standard colorimetric method ([APHA, 1995](#)) and Hach Lange photolab. Nitrate (N-NO₃) was measured by ion chromatography (A-732 Metrohm® separation-center based system using anion column Metrosep A-SUPP-5-150®). Precision was 10% for all dissolved nutrient analysis.

2.3.4. Grain size distribution analyses

Grain size distribution was measured on bulk sub-samples using a laser diffraction sizer after a 3 min ultrasonic agitation (Malvern Mastersizer 2000, IGE-OSUG Laboratory, Grenoble, France).

2.4. Geochemical and ecotoxicological indexes

2.4.1. Enrichment factor

Assessment of the metal enrichment degree in sediments was undertaken using the enrichment factor (EF). The index allows differentiating natural geochemical background to anthropogenic inputs ([Zhang and Liu, 2002](#)). The enrichment factor is defined as the ratio of Al normalized metal concentrations in sediments over Al normalized ratio in a geochemical background reference. Normalization to Al is used to compensate natural variability due to grain-size variations (e.g. mineral composition) and to detect any anthropogenic metal contributions ([Loring, 1991](#); [Chapman and Wang, 2001](#)). [Zhang and Liu \(2002\)](#) defined that an EF value between 0.5 and 1.5 suggests natural weathering processes while a value of EF > 1.5 suggests trace metals being delivered from non-crustal materials corresponding to enrichment from anthropogenic sources. More precisely, [Birth \(2003\)](#) defined that 1.5 < EF < 3 is minor enrichment, 3 < EF < 5 is moderate enrichment, 5 < EF < 10 is moderately severe enrichment, 10 < EF < 25 is severe enrichment, 25 < EF < 50 is very severe enrichment, and finally that EF > 50 is extremely severe enrichment.

2.4.2. Geoaccumulation Index (Igeo)

The degree of metal enrichment was also assessed using the Geoaccumulation Index (Igeo, [Müller, 1979](#)) originally defined for metal concentrations in the <2 mm fraction with respect to the background value B_n as a 'pre-civilisation' value for the study area. The Igeo calculation is based on the following formula:

$$I_{geo} = \log_2 \frac{C_n}{1.5 \cdot B_n}$$

where C_n is the measured concentration in the sediment for metal n, B_n is the background value for the metal n, and factor 1.5 is used because of possible variations in background data due to lithological variations. The geoaccumulation Index includes seven grades: Igeo ≤ 0 Uncontaminated; 0 < Igeo < 1 uncontaminated to moderately contaminated; 1 < Igeo < 2 moderately contaminated; 2 < Igeo < 3 moderately to strongly contaminated; 3 < Igeo < 4 strongly contaminated; 4 < Igeo < 5 strongly to extremely contaminated; 5 < Igeo extremely contaminated.

2.4.3. Sediment quality guideline

A sediment quality guideline (SQG) has been developed for singular ecosystems with freshwater or marine sediments. In marine ecosystems, the mean Effect Range Median quotients (m-ERM-

q) is a pollutant-specific index from the SQG obtained in laboratory experiments using amphipod organisms (Long et al., 1998). It takes into account mixtures of contaminants, including trace metals, present in sediment samples, and provides a management tool for assessing sediment quality in terms of adverse biological effects. The m-ERM-q calculation is based on:

$$m-ERM-q = \frac{\sum_{i=1}^n \frac{C_i}{ERM_i}}{n}$$

where C_i is the concentration of the pollutant i in the sample, ERM_i is the experimentally defined effect concentration for the pollutant i and n is the number of studied pollutants i . Four classes of toxicity probability for biota are then defined: low (m-ERM-q < 0.1), low-medium (m-ERM-q: 0.11–0.5), medium–high (m-ERM-q: 0.51–1.5) and high priority sites (m-ERM-q > 1.5) (Long et al., 1998). The m-ERM-q index is derived from the concept of effect range-low (ERL i.e. 10th percentile of the effect dataset) and effect range-median (ERM i.e. 50th percentile of the effect dataset) defined by Long et al. (1995) respectively as the concentrations below which adverse effects are not expected to occur, above which adverse effects are expected to occur.

In freshwater ecosystems, MacDonald et al. (2000) evaluated a consensus-based SQG for 28 chemicals (i.e. metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and pesticides) and developed the threshold effect concentration (TEC) and probable effect concentration (PEC) indexes for freshwater sediment. The TEC was defined as the concentration below which adverse effects are not expected to occur and the PEC as the concentration above which adverse effects are expected to occur more often than not. Based on the mean Effect Range Median quotient (m-ERM-q; Long et al., 1998), a mean PEC quotient (m-PEC-q) was defined by MacDonald et al. (2000) as predicting the absence of toxicity if mean PEC quotient is lower than 0.5 and a high probability of sediment toxicity if the mean PEC quotient is higher than 0.5.

2.5. Statistical analysis

The Pearson correlation coefficient matrix and one-way ANOVA at probability level $p < 0.05$ (to test seasonal effect) were performed using statistical package software (SPSS; version 23).

3. Results & discussion

3.1. River water mass characteristics

Physico-chemical parameters vary along the river and between the seasons (Table 1b). The dry season is characterized by higher water temperature (approximately $2\text{ }^{\circ}\text{C}$) and a saline water intrusion up to the MD7 site (the intrusion being downstream during rainy season). The pH and DO values vary with opposite seasonal trends: pH being more acidic during the rainy season whereas water is less oxygenated during the dry season. The Tien River acidification is closely related to the leaching of the surrounding acid sulfate soils during rainy seasons (Minh et al., 1997) while the decreasing oxygenation during the dry season could be the result of enhanced organic matter degradation along the river network (Trinh et al., 2012). The local DO decrease observed at MD6 during both seasons is the likely result of direct domestic and urban discharges from My Tho City (230 000 inhabitants; Table 1a). During the dry season, the P- PO_4 concentrations are quite low but increases locally in nearby urban centres (between MD-2 and MD-4; Table 1a, 2) while the N- NO_3 concentrations are likely the result of intense agricultural activity along this river (Table 2). In the estuarine environment, (MD-8 to MD-10) N- NH_4 concentrations

(Table 2) increased two fold and could be related to intense aquaculture activity (Table 1a). During the rainy season, different distributions are observed with lower nutrient concentrations highlighting the strong dilution capacity of the Mekong River. Despite significant progress in the development of the wastewater management sector in Vietnam, 60% of urban wastewater is connected to sewerage and only 10% of this collected wastewater is treated (World Bank, 2013). Specifically in the Mekong Delta, water quality management is an urgent problem with regards the multiple sources of pollution including domestic, urban, agricultural, industrial and aquaculture sources (Waibel et al., 2012). A dramatic rise in nutrient concentrations has also been observed on a global scale in the last decade, in response to land use changes and urban development, in rivers from South-East Asia countries such as in the lower Mekong basin in Laos (Li and Bush, 2015), the Red River watershed in Northern Vietnam (Garnier et al., 2015), and in the Yangtze River in China (Li et al., 2011).

In the Tien River, SPM concentrations are low during both seasons (Table 3) and in a similar range as previously reported by Noh et al. (2013). Higher concentrations were measured during the rainy seasons and are related to enhanced SPM transfer in the Mekong watershed (Loisel et al., 2014). During the dry season, the low SPM concentrations increased sharply in the brackish zone (Table 3) suggesting estuarine flocculation processes (Lefebvre et al., 2012). The POC_{SPM} contents vary from 1.1% to 9.0% (Table 3) and are in the same range as previously observed by Noh et al. (2013). During the dry season, the higher POC_{SPM} contents measured in the riverine part support our hypothesis regarding the importance of local urban wastewater release into the river. Then, in the brackish zone, POC_{SPM} decreased (i.e. MD6 to MD9; Table 3) suggesting both enhanced organic degradation processes in the estuarine water column and dilution of fluvial particles by organic-depleted resuspended sediment (Etcheber et al., 2007; Statham, 2012). During the rainy season, the low POC_{SPM} content (mean of 1.3%) associated with high SPM concentration levels (Table 3) is likely related to the terrigenous origin of the SPM. This minimum POC_{SPM} value, defined as the terrigenous signature, can range from 0.5% in a very erodible watershed (e.g. in the Taiwan watershed; Kao and Liu, 1997) and up to 5% in an equatorial forested watershed (e.g. the Congo River Coyne et al. (2005).

3.2. Filtered and suspended particulate metal dynamics in the Tien River

Filtered (V_F , Cr_F , Co_F , Ni_F , Cu_F , Zn_F , As_F , Mo_F , Cd_F , Pb_F , U_F) and particulate (V_{SPM} , Cr_{SPM} , Co_{SPM} , Ni_{SPM} , Cu_{SPM} , Zn_{SPM} , As_{SPM} , Mo_{SPM} , Cd_{SPM} , Pb_{SPM} , Al_{SPM} , Fe_{SPM} , Mn_{SPM}) trace metal concentrations measured in the Tien River (Table 2; Table 3) are within the mean world rivers dissolved (Gaillardet et al., 2014) and particulate (Viers et al., 2009) values and in the same concentration range as previously reported in the Mekong Delta (Cenci and Martin, 2004) and in the Lower Mekong River (Gaillardet et al., 1999). In particular, As_F concentrations remain far below the concentrations previously reported in the Mekong Delta aquifers (Berg et al., 2007). The comparison to main Asian tropical rivers (Table 4) such as the Yangtze River Estuary (Yang et al., 2014), the Huanghe River Estuary (Wang et al., 2016a) and the Pearl River Estuary (Zhang and Liu, 2002; Zhang et al., 2013) demonstrates that the Mekong Delta is in the low range of both dissolved and particulate concentrations, confirming the previous statement of Cenci and Martin (2004) on the negligible anthropogenic metal inputs to this system. The pH, DO and SPM concentrations have a limited effect on the dynamic of Metal_F concentrations ($r = 0.73$, $p < 0.01$ level for Ni_F and SPM only) and $\text{Metal}_{\text{SPM}}$ concentrations ($r = 0.79$ and $r = 0.76$, $p < 0.01$ level for Al_{SPM} and Fe_{SPM} with SPM only). Accordingly, the metal

Table 1b

Measured dissolved oxygen (DO), pH, temperature, conductivity, salinity and SPM concentrations in surface water, grain size distribution and modes of surface sediments at each sampling site during both dry and rainy seasons. (n.d.: not determined).

	Sampling site	D.O. mg L ⁻¹	pH	T °C	Conductivity mS cm ⁻¹	Sal	Grain size distribution			
							D10	D50	D90	mode
March dry season	MD-1	4.82	7.82	31.8	0.216	0.1	2.4	12.6	48.5	uni-modal
	MD-2	4.9	7.61		0.207	0.1	5.6	49.3	117.0	uni-modal
	MD-3	5.02	7.05	30.1	0.21	0.1	4.0	47.2	171.5	bi-modal
	MD-4	5.06	7.44	30.2	0.219	0.1	2.9	39.8	161.4	bi-modal
	MD-5	4.67	7.59		0.212	0.1	4.0	42.3	310.8	bi-modal
	MD-6	3.77	7.58	30.3	0.404	0.1	2.5	15.3	56.7	uni-modal
	MD-7	4.48	7.68	30.5	3.4	1.7	2.5	13.8	56.5	uni-modal
	MD-8	4.31	7.8	30.6	8.33	4.7	2.6	15.9	143.8	bi-modal
	MD-9	6	7.91	n.d.	18.9	11.3	1.7	6.4	24.4	uni-modal
	MD-10	6	8.25	30.2	30.7	19	2.2	16.3	97.9	bi-modal
October rainy season	MD-4	4.88	7.22	27.8	80	0	2.3	11.9	46.2	uni-modal
	MD-5	5.31	7.1	27.7	75.5	0	1.7	7.6	31.9	uni-modal
	MD-6	4.63	6.95	27.9	82.5	0	2.7	16.4	57.8	uni-modal
	MD-7	5.41	7.1	27.8	84.7	0	1.5	6.5	21.2	uni-modal
	MD-10	6.6	7.4	27.9	3470	1.8	2.1	10.7	58.0	uni-modal

Table 2

Measured filtered metal (V_F, Cr_F, Co_F, Ni_F, Cu_F, Zn_F, As_F, Mo_F, Cd_F, Pb_F, U_F) and nutrient (P-PO₄, NeNH₄) concentrations in surface water at each sampling site during both dry and rainy seasons. (n.d.: not determined).

	Sites	V _F	Cr _F	Co _F	Ni _F	Cu _F	Zn _F	As _F	Mo _F	Cd _F	Pb _F	U _F	P-PO ₄	NeNH ₄	NeNO ₃
		units	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹
March dry season	MD-1	1.37	0.092	0.061	0.46	0.63	11.8	1.63	0.35	0.005	0.041	0.38	0.02	0.06	1.5
	MD-2	1.32	0.066	0.042	0.62	n.d.	9.3	1.60	0.36	0.010	0.061	0.38	0.03	0.07	1.7
	MD-3	1.28	0.044	0.040	0.46	0.78	14.6	1.50	0.36	0.009	0.017	0.36	0.22	0.03	1.8
	MD-4	1.16	0.062	0.047	0.49	1.06	30.2	1.30	0.32	0.022	0.246	0.27	0.04	0.06	2.0
	MD-5	1.30	0.007	0.031	0.44	0.64	11.7	1.38	0.32	0.004	0.013	0.18	0.02	0.06	2.2
	MD-6	2.31	0.109	0.064	0.48	0.99	72.3	1.38	0.27	0.007	0.141	0.11	0.01	0.05	2.8
	MD-7	n.d.	0.978	0.067	0.70	0.99	7.1	n.d.	0.67	0.008	0.061	0.16	0.01	0.07	1.5
	MD-8	1.43	0.157	0.046	0.52	1.22	18.3	1.16	1.63	0.012	0.080	0.51	0.01	0.14	1.4
	MD-9	1.67	0.109	0.041	0.61	1.21	12.9	1.36	3.56	0.013	0.039	1.19	0.01	0.14	n.d.
	MD-10	1.95	0.138	0.038	0.73	1.41	32.2	1.47	6.37	0.024	0.035	2.04	0.01	0.16	n.d.
October rainy season	MD-4	1.41	0.059	0.476	3.26	2.90	29.9	0.93	0.12	<0.01	0.804	0.05	0.01	0.07	0.2
	MD-5	1.38	0.035	0.524	2.22	0.96	37.4	0.88	0.52	<0.01	0.116	0.04	0.01	0.03	0.2
	MD-6	1.34	0.313	1.298	3.10	1.09	9.9	0.84	0.13	<0.01	0.017	0.04	0.02	0.03	0.2
	MD-7	1.28	0.071	0.442	2.30	0.96	20.5	0.77	0.13	<0.01	0.063	0.05	0.01	0.02	0.2
	MD-10	1.47	<0.01	1.332	3.73	3.56	4.9	2.57	0.39	<0.01	<0.01	0.09	0.01	0.02	0.2

Table 3

Measured particulate metal (V_{SPM}, Cr_{SPM}, Co_{SPM}, Ni_{SPM}, Cu_{SPM}, Zn_{SPM}, As_{SPM}, Mo_{SPM}, Cd_{SPM}, Pb_{SPM}, Al_{SPM}, Fe_{SPM}, Mn_{SPM}) and particulate organic carbon (POC) concentrations in surface suspended sediment at each sampling site during both dry and rainy seasons. (n.d.: not determined).

	Sites	V _{SPM}	Cr _{SPM}	Co _{SPM}	Ni _{SPM}	Cu _{SPM}	Zn _{SPM}	As _{SPM}	Mo _{SPM}	Cd _{SPM}	Pb _{SPM}	Al _{SPM}	Fe _{SPM}	Mn _{SPM}	POC _{SPM}	SPM
		units	Mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	%
March dry season	MD-1	n.d.	18.0	6.8	12.1	13.9	n.d.	n.d.	n.d.	n.d.	16.0	12 760	15 105	675	9.0	7
	MD-2	n.d.	31.0	15.1	23.3	24.4	168	n.d.	n.d.	n.d.	27.8	21 827	27 909	1132	6.2	9
	MD-3	n.d.	27.8	13.3	20.2	21.1	n.d.	n.d.	n.d.	n.d.	24.0	20 281	25 035	1005	5.4	8
	MD-4	n.d.	36.2	15.7	24.7	92.1	n.d.	n.d.	n.d.	n.d.	29.0	23 538	30 528	753	3.5	11
	MD-5	n.d.	38.0	17.7	28.0	27.1	335	n.d.	n.d.	n.d.	36.6	29 967	35 531	678	5.5	11
	MD-6	n.d.	43.3	20.4	32.4	25.9	575	n.d.	n.d.	n.d.	27.9	34 044	35 902	569	1.7	43
	MD-7	n.d.	41.1	23.1	34.5	27.5	229	n.d.	n.d.	n.d.	30.9	29 814	36 704	1147	1.4	133
	MD-8	n.d.	39.7	18.5	29.2	33.6	92	n.d.	n.d.	n.d.	23.5	25 199	31 043	658	1.4	63
	MD-9	n.d.	61.6	28.2	43.4	31.0	n.d.	n.d.	n.d.	n.d.	39.0	39 778	47 598	1148	2.2	28
	MD-10	n.d.	41.6	18.4	29.8	29.0	n.d.	n.d.	n.d.	n.d.	25.2	26 304	31 389	721	2.7	30
October rainy season	MD-4	125	23.4	14.1	27.3	41.0	147	21.6	0.45	0.17	32.7	99 599	52 591	297	1.1	154
	MD-5	122	38.9	14.3	33.0	40.6	144	22.1	0.58	0.17	33.4	94 222	53 578	490	1.2	171
	MD-6	136	34.8	16.4	34.4	47.1	287	24.3	0.61	0.28	37.0	106 488	58 989	552	1.3	148
	MD-7	121	n.d.	13.4	16.1	36.9	139	21.4	0.27	0.23	32.9	104 556	54 938	85	1.4	128
	MD-10	134	21.7	14.3	26.2	43.0	151	25.2	0.80	<LD	36.6	114 618	58 361	141	1.3	80

partitioning in the river water column was firstly assessed by the partitioning coefficient K_d defined as the ratio of $\text{Metal}_{\text{SPM}}$ over Metal_F (Turner et al., 1993). The $\text{Log}K_d$ (Table 5) are stable in the Tien River and do not present any significant variation with pH, DO and SPM ($p > 0.05$). Consequently, the metal partitioning was

assessed in a different way by taking into account the total concentration relative to the volume of water, expressed in Mg L^{-1} (i.e. the particulate concentrations were multiplied to the SPM concentrations and summed to the dissolved concentrations). The total concentrations expressed in Mg L^{-1} (Fig. 2) vary through the Tien

Table 4 Dissolved and particulate (in both suspended and deposited sediment) trace metal concentrations of main Asian tropical rivers. (References cited: [Cenci and Martin, 2004](#); [Yang et al., 2014](#); [Wang et al., 2016b](#); [Zhang et al., 2013](#); [Zhang and Liu, 2002](#); [Wang et al., 2015, 2017](#); [Datta and Subramanian, 1998](#)).

Location	V	Cr	Co	Ni	Cu	Zn	As	Mo	Cd	Pb	Hg	References
<i>Dissolved concentrations ppb, min-max</i>												
Mekong Delta	1.2e2.3	0.01	0.03	0.44	0.6	4.9e72	0.8e2.6	0.12e6.4	0.010	0.01		Current study
Mekong Delta		0.31	0.07	0.73	3.6				0.024	0.80		Cenci and Martin, 2004
Yangtze River Estuary		0.03e23	0.01	0.06	0.1e44	0.3e130	0.1		0.001e1.97	0.01		Yang et al., 2014
Huanghe River Estuary			23.3	25.9	0.9e6	1.2e35	1.4e2.5		0.003e0.32	0.04e8.2		Wang et al., 2016a
Pearl River Estuary					0.3	3.7e36	0.2e8.2		0.001e0.3	0.19		Zhang et al., 2013
					3.3					4.58		
<i>Suspended particulate concentrations ppm, min-max</i>												
Mekong Delta	121	18e62	6.8e28	12e43	14e92		21e25	0.27	0.17e0.28	16e39		Current study
Mekong Delta		136						0.80				
Yangtze River Estuary		9e158	1e41	7e123			2e73			4e84		Cenci and Martin, 2004
Huanghe River Estuary		45e1273	4.1e71	12e204	22	54	3.9		0.11e54.9	6e1445		Yang et al., 2014
Pearl River Estuary					0.6e41	1.5e88	0.1e7.9		0.001e0.23	2e79	0.001	Wang et al., 2016a
											0.224	
		71	18	62	51	212			0.82	75		Zhang and Liu 2002 mean only
<i>Surface sediment particulate concentrations ppm, min-max</i>												
Mekong Delta	39e161	24e87	7.4e22	13e48	7.1e36		8.4e21	39e161	0.08e0.31	12e31	0.023	Current study
											0.106	
Yangtze River Estuary		50e123		20e42	9.7e49	46e127	5.0e17		0.07e0.71	15e45		Wang et al., 2015
Huanghe River Estuary		14e64			1.2e47	30e81	4.1e23		0.04e0.2	3.2e34	0.012	Wang et al., 2017
											0.379	
Pearl River Estuary					10e89	52e186	10e23		0.04e0.84	20e64		Zhang et al., 2013
Ganges River	36e50	55e146		18e39	15e31	53e117				14e24		Datta and Subramanian, 1998
Brahmaputra River	43e86	55e160		18e51	15e51	48e149				10e38		Datta and Subramanian, 1998

River and are higher during the wet season than during the dry season (ANOVA, $p < 0.01$ for Cr, Cu and Pb) suggesting enhanced metal load transport during the rainy season towards the ocean. Furthermore, particulate concentrations expressed in mg L^{-1} vary from site to site and are closely related to SPM concentration variations ([Fig. 2](#); $p < 0.01$ for total V, Cr, Co, Ni, Cu and Pb during both seasons). This pattern supports that SPM concentrations control the load of total metal concentrations in the Mekong Delta during both dry and wet seasons, as observed in the Yangtze River Estuary ([Yang et al., 2014](#)). Given the perspective of increased hydropower dam constructions on the main channel and its tributaries, the resulting decrease of sediment load will probably affect the trace metal load in the Mekong Delta. During transportation, the particulate phase is the dominant phase for V, Cr, Co, As and Pb ([Fig. 2](#)) while the dissolved metal fraction dominates for Mo, Ni and Cu in the riverine part, and only for Mo in the estuarine part ([Fig. 2](#)). Dissolved metal concentrations vary along the estuarine salinity gradient ([Table 2](#)) resulting in high particulate-dissolved reactivity associated with physical, chemical and biological processes in the mixing zone ([de Souza Machado et al., 2016](#)). This reactivity can be approached by the mixing diagram (e.g. [Liss, 1976](#); [de Souza Machado et al., 2016](#)), which reflects the concentration of an element over salinity between two endmembers: the river and the ocean (i.e. data from the South China Sea ([Cenci and Martin, 2004](#); [Wang et al., 2012b](#); [Wen et al., 2006](#)) and from mean ocean values ([Nozaki, 2001](#))). When the concentrations follow the theoretical dilution line between the two endmembers, the element is thus controlled by the physical mixing and its behaviour is defined as conservative. Such conservative behaviour is observed for U_F , V_F and Mo_F in the Tien River ([Fig. 3](#); $p < 0.01$ for U_F and Mo_F with salinity). In most estuaries that have

been studied, U_F behaves conservatively ([Windom et al., 2000](#); reference within; [Strady et al., 2009](#)) while such behaviour is less usual for Mo_F and V_F (e.g. in the Chao Phraya Estuary; [Dalai et al., 2005](#)). Both Mo_F and V_F can be affected by intra-estuarine transformation processes like SPM or sediment sorption/desorption reactions and biological uptake as observed in the Gironde Estuary ([Strady et al., 2009](#)) and in the Taiwan Strait ([Wang et al., 2016a](#)). Thus, this non-conservative behaviour deriving from the theoretical dilution line (i.e. gain or loss of dissolved element), illustrates a higher reactivity between the dissolved and particulate phase (e.g. SPM or sediment). In the Tien River, gains of Ni_F , Cu_F , As_F , Co_F and Cd_F were observed ([Fig. 3](#)) suggesting intense desorption processes from particles occurring in the salinity gradient. This bell-shaped pattern is well documented for Cd_F as a chloride-induced desorption from the suspended sediments and has been previously observed in the Mekong Delta ([Cenci and Martin, 2004](#)) and other estuaries like the Gironde Estuary ([Kraepiel et al., 1997](#); [Dabrin et al., 2009](#)), the Pearl River ([Wang et al., 2012a](#)), the Saigon River ([Strady et al., 2017](#)) and the Huanghe River Estuary ([Wang et al., 2016b](#)). For Cu_F , even if a conservative behaviour is more usual and has been observed in the Mekong Delta (e.g. [Cenci and Martin, 2004](#)), in the Pearl River ([Wang et al., 2012a](#)) and in the Huanghe River estuary ([Wang et al., 2016b](#)), desorption from the reactive particles is the suggested explanation for the bell-shaped pattern observed in the Gironde Estuary ([Kraepiel et al., 1997](#)). In the Tien River, this hypothesis could explain the gain of Cu_F but the absence of significant correlation with SPM concentrations along the system ($p > 0.05$) and between $\text{Log}K_d$ and salinity ($p > 0.05$) does not allow us to make any conclusions on Cu particle reactivity. Unlike previous measurements performed in the Mekong Delta ([Cenci and](#)

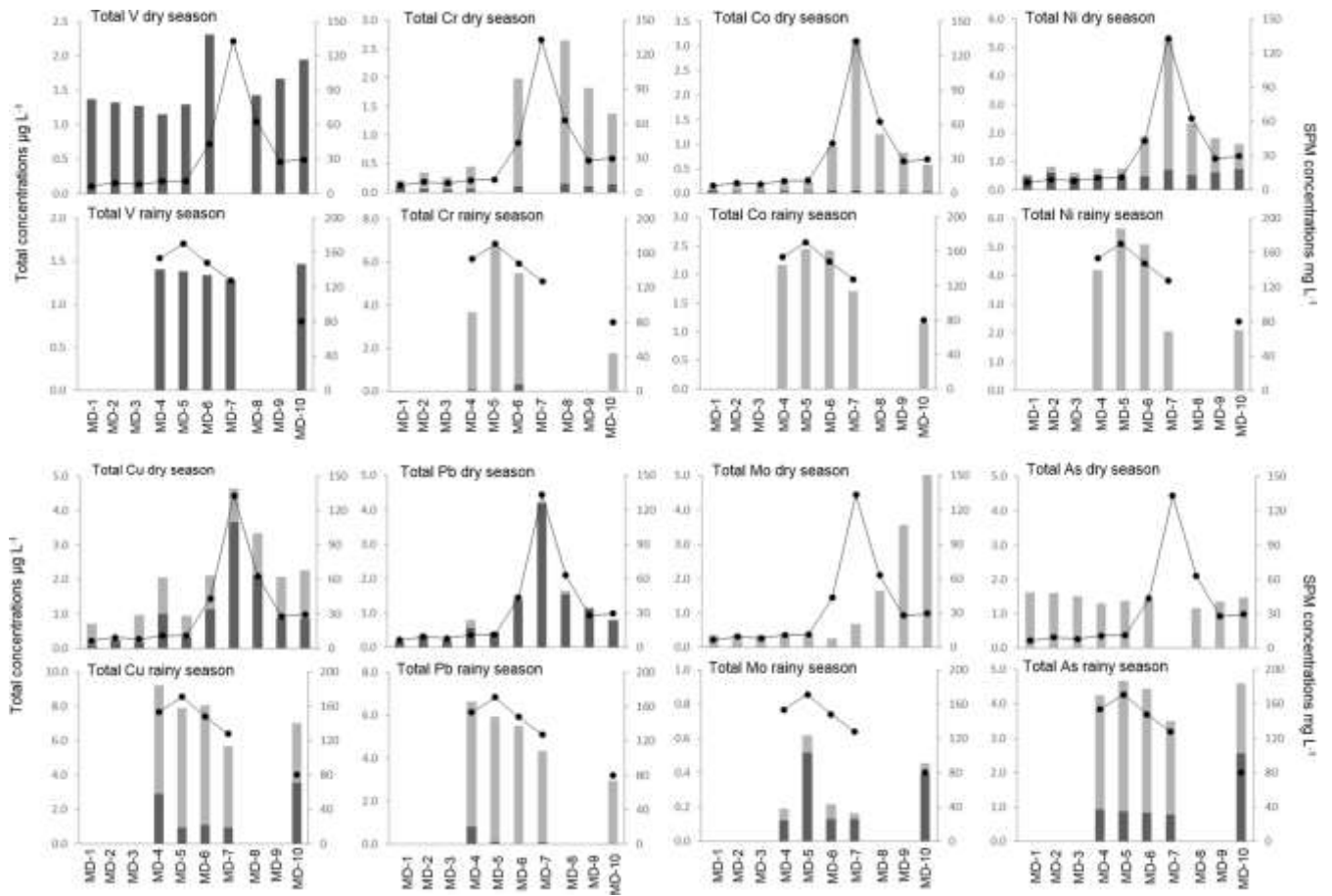


Fig. 2. Spatial variation of calculated total metal concentrations (sum of dissolved and particulate concentrations; V, Cr, Co, Ni, Cu, As, Mo, Pb) expressed in mg L^{-1} and SPM concentrations expressed in mg L^{-1} during both dry and rainy seasons.

(Martin, 2004) and the Huanghe River estuary (Wang et al., 2016b), As_F and Ni_F concentrations increase in the mid salinity range. In the case of As, the linear positive correlation ($r = 0.79$) observed between POC_{SPM} and As_F during the dry season suggests an As release

during organic degradation processes occurring in the estuary (Table 2; 3). For Ni_F , the significant negative correlation with SPM concentrations ($r = 0.74$, $p < 0.01$) suggests desorption from suspended particles along the salinity gradient. This is in accordance

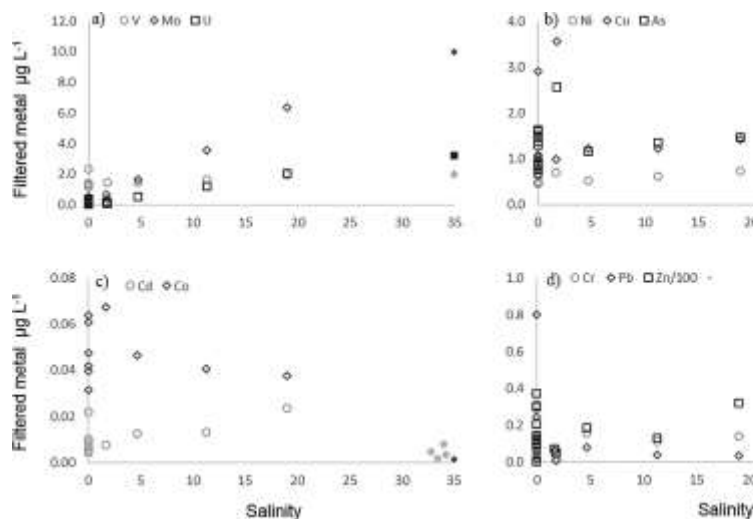


Fig. 3. Filtered metal concentrations along the salinity gradient a) V, Mo, U; b) Ni, Cu, As; c) Cd, Co; d) Cr, Pb and Zn (expressed as Zn/100) during both seasons. The marine endmember is characterized according to data from Wang et al., 2012b; Wen et al., 2006; Censi and Martin, 2004, Nozaki, 2001.

with reported laboratory experiments and modelling of metal desorption kinetics which highlight Ni desorption from polluted riverine and estuarine sediments (Millward and Liu, 2003). However, the impact of desorption on observed non-conservative behaviour was minimized by the authors because of the low Ni kinetic desorption and the non-attempt of sorption equilibrium in a dynamic estuarine environment. Finally, concerning Cr_F, Zn_F and Pb_F, the high variability of measured concentrations in the riverine part make it difficult to get a proper river endmember and therefore to determine the gain or loss of metal towards the ocean. Further investigation is needed to find the origin of this high variability, either from anthropogenic inputs (e.g. small localised industrial activity such as electronics, textiles and construction) or from acid sulfate soil leaching.

3.3. Factors controlling metal distributions in the Tien River surface sediments

The surface sediments of the Tien River present a grain size distribution dominated by silt classes (54–87%) and a median grain-size (D50) comprised between 6 and 49 μm (Table 1b). The grain size distributions varied from site to site and with seasons, without exhibiting a specific spatial pattern from the river to the coastline. The POC_{SED} content ranges from 0.2 to 1.5% (Table 6). Metal_{SED} concentrations measured in the Tien River (Table 6) are in the same range as previously observed in this system (Cenci and Martin, 2004; Noh et al., 2013) and are in the low concentration range of the main Asian Rivers (Table 4) such as the Yangtze River Estuary (Wang et al., 2015), the Huanghe River Estuary (Wang et al., 2017), the Pearl River Estuary (Zhang et al., 2013), the Ganges-Brahmaputra Rivers (Datta and Subramanian, 1998) and including the Saigon River (Strady et al., 2017). Cenci and Martin (2004) observed that Metal_{SED} in the Mekong Delta varies spatially but not seasonally. In this study, we observed the same pattern except for Cu_{SED} and Zn_{SED} (ANOVA, p > 0.05).

In surface sediments, the Pearson correlation matrix applied to both seasons highlights positive correlations between the entire Metal_{SED} set (including Al_{SED}, Mn_{SED} and Fe_{SED}), and also between Metal_{SED} and POC_{SED} (Table 7). These results support that (i) particle-size, (ii) POC content and/or (iii) Fe, Al and Mn oxy(hydr) oxides are the major carrier phases controlling the spatial distribution of particulate trace metals in this system. Firstly, the small sized particles' highly specific surface plays a major role in metal retention (e.g. Foerstner and Wittmann, 1979; Loring, 1991; Jung et al., 2014). Secondly, although POC_{SED} content is low (0.2–1.5%; Table 6), its strong correlation with Hg_{SED}, As_{SED} (r = 0.83 and 0.84, for Hg and As respectively p < 0.01 Table 7) and Co_{SED}, Cu_{SED}

(r = 0.76 and 0.76 p < 0.01 Table 7) suggest that organic matter is a major carrier for these elements, as it has been observed for Cu in the Saigon River sediments (Strady et al., 2017) and for Hg in the Lower Mekong Basin sediments (Noh et al., 2013; Guedron et al., 2014). In the particular case of As, the positive correlation observed between As_{SED} and POC_{SED} is unusual since As has been documented to be primarily controlled by sorption onto metal oxide surfaces in natural environments (e.g. Redman et al., 2002) although it has been reported that As was sequestered as organo-arsenic complexes in organic rich sediments (Baruah et al., 2003). However, the co-precipitation of microbially synthesized arsenopyrites on organic matter surfaces or on the formation of organo-arsenic complexes (Paikaray et al., 2005) can both explain the unusual observed correlation.

Finally, Metal_{SED} are positively correlated to Fe_{SED} and Mn_{SED}, with a significant correlation (p < 0.01) between Fe_{SED} and the following Metal_{SED} in the specific sequence: Pb_{SED} > Ni_{SED} > As_{SED} > Co_{SED} > Cu_{SED} > Al_{SED} > Hg_{SED} > Mn_{SED} > Cr_{SED} > Zn_{SED} > V_{SED} and between Mn_{SED} and the following Metal_{SED} in the specific sequence: Fe_{SED} > Pb_{SED} > Co_{SED} > Hg_{SED} > Cu_{SED} > Al_{SED} > As_{SED} > Zn_{SED} > Ni_{SED} > Cr_{SED} > V_{SED}. The sorption selectivity on most metal-oxide minerals determined by Schultze et al. (1987) follows the sequence Cr ≤ Pb ≤ Cu > Co ≤ Zn > Ni ≤ Cd, with some distinct differences such as the preference of MnO₂ for Co (Smith, 1999). The sequence based on Metal_{SED} and Fe_{SED}/Mn_{SED} correlation in the Tien River surface sediments differs and exhibits a specific pattern, which could be related to the presence and characteristics of the surrounding acid sulfate soils (Minh et al., 1997). The oxidation of these soils causes metals to be redistributed from the "pyritic" and "organic" fractions to the "acid-soluble" fraction (Claff et al., 2011). Then, the subsequent acidification, due to exceedance of the acid neutralizing capacity of the soil, drives the release of metals to the "labile" fraction (Claff et al., 2011). Thus, the oxidation and acidification of sulfidic soil could lead to changes in metal mobility and consequently to metal sorption phases and distribution in the sediments. In the Tien River, the comparison of Metal_{SED} with Metal_{SPM} for both seasons gives similar concentration ranges (Tables 3 and 6), except for Cr and Pb which present higher concentrations in sediments and SPM respectively. Such differences for Cr and Pb are likely related to a change in speciation and carrier phases in the sediment resulting in diagenetic processes (e.g. a drop in pH and Eh). Because Cr is sensitive to redox states and oxygenation levels, the difference between measured Cr_{SED} and Cr_{SPM} could originate from differences between redox and oxygen values in the two compartments, even though they were not measured at the water-sediment interface. Unlike in the sediment no significant

Table 5
LogKd (Cr, Co, Ni, Cu, As, Mo, Pb) at each sampling site during both dry and rainy seasons. (n.d.: not determined).

	Sites	LogKdCr	LogKdCo	LogKdNi	LogKdCu	LogKdAs	LogKdMo	LogKdPb
March dry season	MD-1	5.3	5.0	4.4	4.3	n.d.	n.d.	5.6
	MD-2	5.7	5.6	4.6	n.d.	n.d.	n.d.	5.7
	MD-3	5.8	5.5	4.6	4.4	n.d.	n.d.	6.1
	MD-4	5.8	5.5	4.7	4.9	n.d.	n.d.	5.1
	MD-5	n.d.	5.8	4.8	4.6	n.d.	n.d.	6.4
	MD-6	5.6	5.5	4.8	4.4	n.d.	n.d.	5.3
	MD-7	n.d.	5.5	4.7	4.4	n.d.	n.d.	5.7
	MD-8	5.4	5.6	4.7	4.4	n.d.	n.d.	5.5
	MD-9	5.8	5.8	4.9	4.4	n.d.	n.d.	6.0
	MD-10	5.5	5.7	4.6	4.3	n.d.	n.d.	5.9
October rainy season	MD-4	5.6	n.d.	n.d.	4.2	4.4	3.6	4.6
	MD-5	6.1	n.d.	n.d.	4.6	4.4	3.0	5.5
	MD-6	5.0	n.d.	n.d.	4.6	4.5	3.7	6.3
	MD-7	n.d.	n.d.	n.d.	4.6	4.4	3.3	5.7
	MD-10	n.d.	n.d.	n.d.	4.1	4.0	3.3	n.d.

Table 6

Measured particulate metal (V_{SED}, Cr_{SED}, Co_{SED}, Ni_{SED}, Cu_{SED}, Zn_{SED}, As_{SED}, Mo_{SED}, Cd_{SED}, Pb_{SED}, Al_{SED}, Fe_{SED}, Mn_{SED}) and particulate organic carbon (POC) concentrations in surface sediment at each sampling site during both dry and rainy seasons. (n.d.: not determined).

	Sites	V _{SED}	Cr _{SED}	Co _{SED}	Ni _{SED}	Cu _{SED}	Zn _{SED}	As _{SED}	Mo _{SED}	Cd _{SED}	Pb _{SED}	Hg _{SED}	Al _{SED}	Fe _{SED}	Mn _{SED}	POC _{SED}	
		units	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	%
March dry season	MD-1	110	71.4	16.7	37.0	36.2	171	19.0	0.57	0.31	30.4	0.087	79 626	46 884	1237	1.2	
	MD-2	65	48.0	11.0	22.6	20.7	110	11.3	0.46	0.17	16.8	0.047	44 947	28 627	642	0.6	
	MD-3	70	47.2	11.1	24.4	20.7	109	12.2	0.28	0.20	18.1	0.053	56 738	31 103	714	0.8	
	MD-4	39	24.5	7.4	13.4	7.1	64	8.4	0.07	0.08	12.2	0.023	32 926	19 808	287	0.2	
	MD-5	69	79.1	15.7	33.1	18.6	114	12.4	4.88	0.19	19.9	0.046	54 501	34 035	942	0.7	
	MD-6	81	78.0	17.0	37.4	33.5	169	17.3	0.66	0.22	29.5	0.106	57 177	45 837	1132	1.2	
	MD-7	98	76.6	16.6	39.7	28.9	155	18.8	0.88	0.14	25.7	0.074	70 907	47 073	1230	1.2	
	MD-8	88	73.9	14.9	32.9	21.8	135	13.6	0.47	0.13	22.9	0.056	50 708	38 666	825	0.7	
	MD-9	112	87.5	18.1	43.7	30.6	169	18.1	1.38	0.11	27.0	0.075	93 633	49 924	1172	1.1	
	MD-10	68	48.8	15.3	27.5	17.7	117	14.9	0.52	0.11	17.7	0.066	52 346	36 196	827	1.4	
October rainy season	MD-4	161	83.8	21.8	37.7	34.2	256	19.1	0.62	0.24	29.6	0.089	79 857	44 667	1216	1.2	
	MD-5	99	62.5	17.9	39.1	36.2	185	20.5	0.93	0.24	30.6	0.091	75 141	46 466	1328	1.5	
	MD-6	99	66.7	16.3	35.2	29.1	169	18.7	0.66	0.22	27.3	0.071	61 951	41 198	1076	0.8	
	MD-7	120	86.0	17.5	47.7	35.5	184	20.8	0.94	0.27	24.3	0.079	n.d.	41 977	805	1.3	
	MD-10	102	79.0	17.7	39.5	27.8	179	16.2	0.87	0.09	28.1	0.057	71 390	45 932	866	1.0	

Table 7

Pearson matrix correlation of particulate metal (V_{SED}, Cr_{SED}, Co_{SED}, Ni_{SED}, Cu_{SED}, Zn_{SED}, As_{SED}, Mo_{SED}, Cd_{SED}, Pb_{SED}, Al_{SED}, Fe_{SED}, Mn_{SED}; in mg kg⁻¹) and POC_{SED} content (%) in sediment during both seasons.

	V _{SED}	Cr _{SED}	Co _{SED}	Ni _{SED}	Cu _{SED}	Zn _{SED}	As _{SED}	Mo _{SED}	Cd _{SED}	Pb _{SED}	Hg _{SED}	Al _{SED}	Fe _{SED}	Mn _{SED}	POC _{SED}
V _{SED}	1														
Cr _{SED}	.755**	1													
Co _{SED}	.874**	.865**	1												
Ni _{SED}	.770**	.919**	.873**	1											
Cu _{SED}	.811**	.737**	.821**	.862**	1										
Zn _{SED}	.956**	.749**	.922**	.784**	.875**	1									
As _{SED}	.807**	.706**	.851**	.890**	.933**	.850**	1								
Mo _{SED}	-.056	.382	.202	.209	-.065	-.063	-.060	1							
Cd _{SED}	.495	.330	.405	.402	.689**	.517*	.567*	.059	1						
Pb _{SED}	.776**	.753**	.861**	.822**	.925**	.874**	.871**	-.010	.525*	1					
Hg _{SED}	.668**	.619*	.782**	.731**	.903**	.790**	.862**	-.126	.620*	.854**	1				
Al _{SED}	.827**	.739**	.807**	.866**	.821**	.785**	.835**	.074	.359	.808**	.660*	1			
Fe _{SED}	.754**	.826**	.888**	.908**	.882**	.810**	.890**	.038	.346	.931**	.830**	.878**	1		
Mn _{SED}	.682**	.692**	.837**	.748**	.831**	.756**	.829**	.170	.505	.887**	.836**	.830**	.893**	1	
POC _{SED}	.596*	.531*	.756**	.729**	.759**	.662**	.837**	-.054	.406	.666**	.828**	.696**	.786**	.745**	1

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

correlation was observed between Fe_{SPM} and Cr_{SPM} although Fe concentrations are in the same range in both compartments. The change of affinity with Fe should be emphasized during field studies and/or experiments to point out the role of redox processes on Cr partitioning. The observed lower Pb_{SED} concentrations when compared to Pb_{SPM} could be the result of intense sediment lixiviation by estuarine and marine waters leading to increasing Pb mobility from the sediment to the dissolved phase as it has been observed in the Yangtze River Estuary (Zhao et al., 2013). This hypothesis cannot be supported in the Tien River.

3.4. Risk assessment of Tien River surface sediments

To assess the degree of metal enrichment in the surface sediments of the Tien River we compared two geochemical indexes: the Enrichment Factor (EF) and the Geoaccumulation Index (I_{geo}) (see material and method 2.3.), calculated for each site and metal. Globally, the calculated EF at all sites (Table 8) evidences none to minor enrichment for V, Cr, Co, Ni, Cu, Mo, Cd, Pb and Hg (EF < 1.5), moderate enrichment for Zn (3 < EF < 5), and moderately severe to severe enrichment for As (5 < EF < 25). The calculated I_{geo} at all sites (Table 8) demonstrates uncontaminated sediment to minor contamination for V, Cr, Co, Ni, Cu, Mo, Cd, Pb and Hg (I_{geo} < 1), moderate contaminated sediments for Zn (1 < I_{geo} < 2), and

moderate to strong contaminated sediment for As (2 < I_{geo} < 4). Thus, these two indexes are showing a Zn_{SED}, and to a greater extent an As_{SED} enrichment or contamination issue in this environment. First of all, we would like to point out that the index conclusions strongly depend on the background values chosen, i.e. the UCC (Wedepohl, 1995) in the present study. In the case of the Mekong River watershed, the geology is diverse and rich making it difficult to get a proper background value. In the absence this background value from a sediment core, Wang et al. (2012b) defined a background value from a geometric means of a high number of samples from the Manwan Reservoir in the Upper Mekong River in China. However, this calculated background value presents high coefficient of variation and low representativity, which can be an issue if applying to the Mekong Delta, considering the distance between this reservoir and the Mekong Delta (up to 2,600 km) and the high number of confluent rivers with specific geological characteristics of the catchment area. Thus, we consider that the UCC is the most suitable background value for this environment. The conclusion of As_{SED} enrichment in the Tien River is coherent with the literature on As contamination in the Mekong Delta, characterized by high levels of As in groundwater and in sediment cores and also by a serious health risk to the local population (e.g. Berg et al., 2007; Buschmann et al., 2008; Hoang et al., 2010). Note that because of the poor Zn accuracy measurement and the consequences on Zn

Table 8
Calculated EF and I_{geo} for surface sediment at each sampling site during both dry and rainy seasons. (n.d.: not determined).

Enrichment Factor		EF _V	EF _{Cr}	EF _{Co}	EF _{Ni}	EF _{Cu}	EF _{Zn}	EF _{As}	EF _{Mo}	EF _{Cd}	EF _{Pb}	EF _{Hg}
March dry season	MD-1	2.0	2.0	1.4	1.9	2.5	3.2	9.2	0.4	3.0	1.7	1.5
	MD-2	2.1	2.4	1.6	2.1	2.5	3.6	9.8	0.6	2.8	1.7	1.5
	MD-3	1.8	1.8	1.3	1.8	2.0	2.9	8.3	0.3	2.7	1.5	1.3
	MD-4	1.7	1.6	1.5	1.7	1.2	2.9	9.9	0.1	1.9	1.7	0.9
	MD-5	1.8	3.2	1.9	2.5	1.9	3.1	8.8	n.d.	2.7	1.7	1.2
	MD-6	2.1	3.0	2.0	2.7	3.2	4.4	11.7	0.6	2.9	2.3	2.6
	MD-7	2.0	2.4	1.6	2.3	2.2	3.2	10.3	0.7	1.5	1.6	1.4
	MD-8	2.5	3.2	2.0	2.7	2.3	4.0	10.4	0.5	2.0	2.1	1.5
	MD-9	1.7	2.1	1.3	1.9	1.8	2.7	7.5	0.8	0.9	1.3	1.1
	MD-10	1.9	2.1	1.9	2.2	1.8	3.3	11.0	0.5	1.5	1.5	1.7
October rainy season	MD-4	3.0	2.3	1.8	2.0	2.3	4.8	9.2	0.4	2.3	1.7	1.5
	MD-5	1.9	1.8	1.6	2.2	2.6	3.7	10.6	0.7	2.5	1.9	1.7
	MD-6	2.3	2.4	1.8	2.4	2.5	4.1	11.7	0.6	2.7	2.0	1.6
	MD-7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	MD-10	2.1	2.4	1.7	2.3	2.1	3.7	8.8	0.7	1.0	1.8	1.1
I_{geo}	I_{geoV}	I_{geoCr}	I_{geoCo}	I_{geoNi}	I_{geoCu}	I_{geoZn}	I_{geoAs}	I_{geoMo}	I_{geoCd}	I_{geoPb}	I_{geoHg}	
March dry season	MD-1	0.5	0.4	-0.1	0.4	0.8	1.1	2.7	-1.9	1.0	0.3	0.0
	MD-2	-0.3	-0.1	-0.7	-0.3	-0.1	0.5	1.9	-2.2	0.1	-0.6	-0.8
	MD-3	-0.2	-0.2	-0.6	-0.2	-0.1	0.5	2.0	-2.9	0.4	-0.5	-0.7
	MD-4	-1.0	-1.1	-1.2	-1.1	-1.6	-0.3	1.5	-5.0	-0.9	-1.1	-1.9
	MD-5	-0.2	0.6	-0.1	0.2	-0.2	0.5	2.1	n.d.	0.3	-0.4	-0.9
	MD-6	0.0	0.6	0.0	0.4	0.6	1.1	2.5	-1.7	0.5	0.2	0.3
	MD-7	0.3	0.5	-0.1	0.5	0.4	1.0	2.6	-1.3	-0.1	0.0	-0.2
	MD-8	0.1	0.5	-0.2	0.2	0.0	0.8	2.2	-2.2	-0.2	-0.2	-0.6
	MD-9	0.5	0.7	0.1	0.6	0.5	1.1	2.6	-0.6	-0.4	0.1	-0.2
	MD-10	-0.2	-0.1	-0.2	0.0	-0.3	0.6	2.3	-2.0	-0.5	-0.5	-0.4
October rainy season	MD-4	1.0	0.7	0.3	0.4	0.7	1.7	2.7	-1.8	0.7	0.2	0.1
	MD-5	0.3	0.3	0.0	0.5	0.8	1.2	2.8	-1.2	0.7	0.3	0.1
	MD-6	0.3	0.3	-0.1	0.3	0.4	1.1	2.6	-1.7	0.5	0.1	-0.2
	MD-7	0.6	0.7	0.0	0.8	0.7	1.2	2.8	-1.2	0.8	-0.1	-0.1
	MD-10	0.4	0.6	0.0	0.5	0.4	1.2	2.4	-1.3	-0.7	0.1	-0.5

concentration over-estimation, the observed Zn_{SED} enrichment may be either over-estimated or may originate from the direct release of industrial and urban wastewater without prior treatment and from urban release such as street and construction dust, house roof made of zinc, or worn out tires.

According to the metal enrichment index results in the Tien River we assessed the ecotoxicological status of its sediments by comparing the measured concentrations with the commonly used

Table 9
Calculated sediment quality guidelines index for freshwater (TEC, PEC, m-PEC-q) and marine water (ERL, ERM, m-ERM-q) ecosystems for surface sediment at each sampling site during both dry and rainy seasons. N is the number of samples comprised between TEC and PEC values and between ERL and ERM values for each metal.

	Cr	Ni	Cu	Zn	As	Cd	Pb	Hg
TEC	43	22.7	32	121	9.8	1.0	35.8	0.18
PEC	111	48.6	149	459	33	5.0	128	1.06
N TEC < Tien River < PEC	11	9	5	9	10	0	0	0
ERL	81	20.9	34	150	8.2	1.2	46.7	0.15
ERM	370	51.6	270	410	70	9.6	218	0.71
N ERL < Tien River < ERM	2	5	1	4	6	0	0	0
	MD-1	MD-2	MD-3	MD-4	MD-5	MD-6	MD-7	MD-10
	2	3	4	5	6	7	8	9
<i>m-PEC-q freshwater sediments</i>								
March 2013 dry season	0.37	0.23	0.24	0.13	0.30	0.37	0.36	
October 2013 rainy season			0.41	0.38	0.35	0.42		
<i>m-ERM-q estuarine and marine sediments</i>								
March 2013 dry season						0.25	0.20	0.26
October 2013 rainy season					0.29			0.25

SQG values for freshwater sediment (i.e MD-1 to MD-7) using TEC, PEC and m-ERM-q indexes and for marine sediments (i.e. MD-7 to MD-10) using ERL, ERM and m-ERM-q indexes (Table 9). Both freshwater and marine sediments exhibit Cd_{SED} , Pb_{SED} , Hg_{SED} concentration ranges below which adverse effects are not expected to occur (lower than TEC and ERL) while Cr_{SED} , Ni_{SED} , Cu_{SED} , Zn_{SED} , As_{SED} exhibit a concentration range above which adverse effects are expected to occur (Table 9). The possible adverse effects of toxic mixtures (Cr, Ni, Cu, Zn, As, Cd, Pb, Hg) evaluated by the calculation of the m-PEC-q and m-ERM-q for freshwater and marine sediments respectively (Table 9), predict an absence of toxicity in the surface freshwater sediments and possible low to medium ecotoxicological potential effects in the estuarine-marine sediments of the Tien River. Because of possible Zn concentration over-estimation, m-PEC-q and m-ERM-q were calculated excluding Zn_{SED} . The two calculations present similar index values (data not shown) suggesting the low contribution of Zn to possible adverse toxic effects. These results support the idea that Mekong River sediments present a low risk to benthic organisms according to metal contamination. However, assumptions regarding ecotoxicological effects should be investigated in further studies combining metal accumulation in sediments and benthic organisms.

4. Conclusions

Despite the development of intense agricultural and aquaculture activity, and of rapid urban growth illustrated by localised high nutrient and organic carbon levels, the Tien River remains in a state of good quality regarding trace metal contamination. Trace metal distributions vary spatially and the metal partitioning appears to be highly dynamic in the salinity gradient of the Mekong Delta. Although the ecotoxicological indexes demonstrated a low to medium contamination of the surface sediments, direct accumulation

measurement in benthic organisms are required to assess the metal risk in biota.

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