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RESEARCH ARTICLE

Assessment and source quantification of heavy metal(loid)s in surface water using multivariate analyses from the Saigon River, Vietnam

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Abstract

The metal concentration in surface water of a river could be affected by season, position, and oceanic process such as tide. The current study aimed to (1) examine the heavy metal(loid) concentration in surface water from the Saigon River as affected by the combination of season, tide, and position and (2) apportion and quantify pollution sources. Ninety-six surface water samples were collected from 13 sites on the River in four campaigns (rainy season + ebb tide, rainy season + flood tide, dry season + ebb tide, and dry season + flood tide). Eight heavy metal(loid)s (Al, B, Bi, Fe, Mn, Pb, Sr, and Zn) were measured and subjected to multivariate analyses. Three-way ANOVA showed that in the rainy season, the total concentration of the metal(loid)s (TCM) in two tides was not clearly different from each other while in the dry season the TCM was significantly higher during the ebb tide than during the flood tide. Principal component analysis/factor analysis and Pearson correlation matrix showed that the TCM could be derived from three main sources, grouped into anthropogenic activities such as industrial, agricultural, and domestic wastes from inside Ho Chi Minh city, and natural origins from lowland area and acid sulfate soil. Three pollution sources explained 70% and 68% of the total variance of TCM in the rainy and dry seasons, respectively. In brief, the metal(loid) concentration was significantly affected by the season and tide and the pollution sources could be derived from inside Ho Chi Minh City and from lowland areas beyond the river estuary.

Keywords Ebb tide · Flood tide · Tidal effect · Seasonal variation · Saigon River

Introduction

Surface water quality of a river is important in affecting the aquatic ecosystem of the water body and human health, where water is used as a drinking water source (Edokpayi et al. 2017). In general, surface water quality is characterized by physical, biological, and chemical properties and heavy metal status. The metals can either serve as essential nutrients for the aquatic biosphere if their concentration is lower than the associated maximum permissible levels or induce toxicity if exceeding specific high thresholds. The metal pollution of river water was studied widely due to their persistence, bioaccumulation, and non-biodegradability (Ayangbenro and Babalola 2017; Bawuro et al. 2018; Jaishankar et al. 2014). The pollution is even more serious in many fast-growing cities in developing countries due to the high discharge of various wastes from rapidly growing industrialization and urbanization (Al-Hussaini et al. 2018; Alsaffar 2018; Karbassi et al. 2007).

For a tidal river, due to the highly dynamic hydrological regime, the metal concentration in surface water can be influenced by various factors, such as season, tide, river position, and pollution source. The season can influence the heavy metal concentration of tidal-river water through various pathways/mechanisms, including transport of the metals from their

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sources to the river, dilution of the element concentration during the rainy season, and an increase of their concentration due to water evaporation occurring during the dry season. Many studies were conducted to address the seasonal variation of the metal concentration in river water (Bhuyan and Bakar 2017; Haque et al. 2005) and two contrastive results were reported. For example, Edokpayi et al. (2017) found that the dry season had higher concentrations of some metals, such as Fe, Mn, Pb, and Zn, than the rainy season had and the higher concentration could be attributed to an evaporative effect of the dry season. Meanwhile, Nienie et al. (2017) reported that the concentration of trace metals was higher in the wet than in the dry season. These inconsistent findings could be the consequence of the difference in studied conditions, suggesting that more studies are needed, especially on a tidal river.

In addition, the concentration of the metals in tidal-river water could be affected by the tide, which can be an ebb or flood tide. The tides can affect the metal concentration of the river through two different ways, which are (1) transporting the pollutants from their sources such as from the upper catchment areas or from the riverside areas to the river through the ebb tide and (2) diluting the pollutant concentration and transporting the metals from the lowland or seawater back to the river through the flood tide. Fortune and Mauraud (2015) concluded that the water quality of Darwin Harbour in Australia varied with the tidal cycle, depending on the water quality parameters and sampling time. Zhang et al. (2015) found that the metal concentration in river water was higher during the ebb tide than during the flood tide, suggesting that the transport of metals from pollution sources to the studied river by the outgoing-river current could happen. The authors also found that the concentration of Zn and Ni was higher in the flood tide than in the ebb tide that was attributed to the difference in pollution sources, derived from a nearby waste-treatment plant. These indicated that the interaction between the tide and studied locations (different pollution sources) could be important in determining the metal concentration in surface water of a tidal river. Moreover, water currents could be affected by both the tide and the season, which interactively influence the heavy metal concentration of a tidal river. These are insufficiently reported and discussed in the literature.

The metal concentration in surface water can vary with river positions, depending on their sources, which can be derived from natural processes and/or anthropogenic activities (Giri and Singh 2013). Basically, almost all heavy metals can be originally derived from natural sources, such as from soil and rock, while human activities can create additional processes to accelerate the distribution of the metals to various environmental compartments (Garrett 2000). For river water, the natural sources can be from soil and rock located in the river catchment, which can be eroded to carry metal-containing materials to the river (Bradl 2005) and the anthropogenic sources can be from municipal, industrial, and agricultural wastes (Hussain et al. 2017; Rai 2008). Transporting the metals from their sources to a tidal river can mainly happen through water flow, which is additionally affected by the season and tide. The interaction of these three factors (season, tide, and river position) would finally determine the metal concentration in the surface water of a tidal river that needs more studies. In addition, identifying and quantifying the pollution sources of the metals are necessary to study for better management.

The Saigon River is a tidal river and is one of the main waterways in Ho Chi Minh City, connecting two areas having specific characteristics related to Al, Fe, and Mn metals from its two ends. Soil from the upper catchment areas of the river is characterized by high concentrations of Al and Fe (Nguyen and Thai 1995) and the soil beyond the estuary is characterized by lowland areas of mangrove forest and acid sulfate soil (high concentration of Al, Fe, and Mn). In addition, the river, running through Ho Chi Minh megacity with rapid development in urbanization and industrialization (Schneider et al. 2017), could be additionally contaminated with heavy metals due to the discharge of a large amount of solid and liquid wastes from the megacity daily. Consequently, the River water was polluted with heavy metals and the downstream water was more polluted than the upstream water (Nguyen et al. 2011). Nevertheless, Strady et al. (2017) highlighted that the dilution effect that occurred in the downstream estuarine area due to the intrusion of seawater could revert the water quality, which was previously degraded by the urban area of Ho Chi Minh City. These may suggest that it is necessary to carry out more studies to clarify the pollution trend along the River. Additionally, these two studies did not quantify the pollution sources of the metals that can be derived from natural processes and anthropogenic activities (Bhuyan and Bakar 2017) and also did not examine the interactive effect of season and tide.

Therefore, the current study was conducted on the tidal Saigon River to (1) examine the heavy metal(loid)s concentration in surface water as affected by the combination of season, tide, and position and (2) apportion and quantify pollution sources of the elements. It was hypothesized that the dry season could result in a higher metal concentration than the rainy season did and that the effect of the season could depend on the tide and river position.

Materials and methods

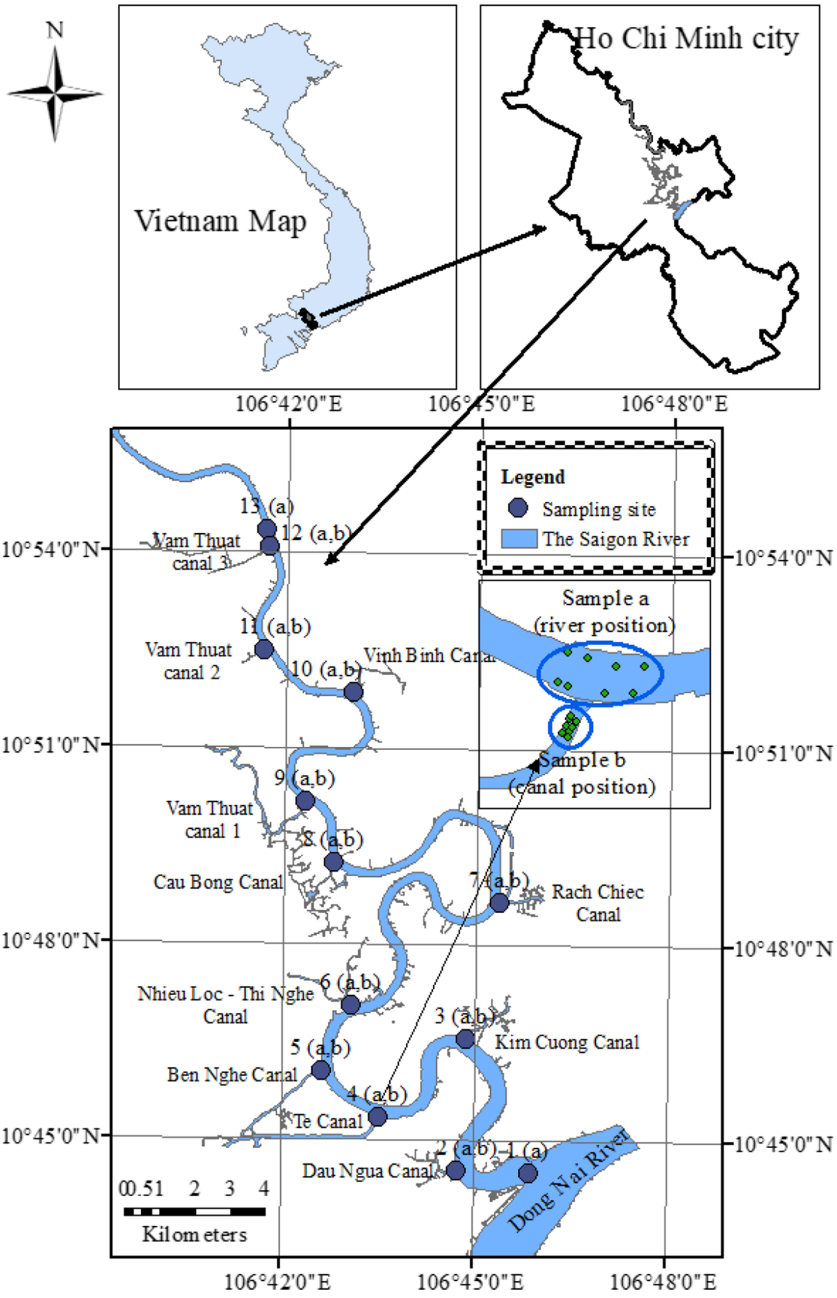
The studied area

The current study was conducted on the Saigon River located in Ho Chi Minh City, Vietnam. Having a total length of around 250 km and a catchment area of around 4717 km^2 (Lahens et al. 2018) (Fig. 1), the River originates from southeastern Cambodia and flows through 3 provinces in Vietnam (Binh Phuoc, Tay Ninh, and Binh Duong) before reaching Ho Chi Minh City for the lower reaches of around 80 km. The River meets the Dongnai River at the low end, the estuary, beyond which is located with lowland areas, including residential areas, industrial zones, paddy fields, mangrove forests, and acid sulfate soil. The River current is affected by the semidiurnal tide regime from the East Sea of Vietnam and varying rainfall of two distinct seasons, the rainy season from May to October and the dry season from December to April (van Emmerik et al. 2018). The annual rainfall of Ho Chi Minh City is around 1868 mm, more concentrated on the rainy season, and the average temperature is 27.4 °C. Ho Chi Minh City is an economic and political center in southern Vietnam, with a fast growth rate of population and industrialization recently. The City is situated on a relatively flat topography with a dense hydrological waterway network (around 700 km length). More information about the Saigon River and Ho Chi Minh City can be seen in the studies of Lahens et al. (2018) and Schneider et al. (2017).

Experimental factors and setup

Three experimental factors were examined, including season, tide, and river position. Thirteen sampling sites were

Fig. 1 Sampling sites and map of the Saigon River in Ho Chi Minh City, Vietnam



examined and positioned to take water samples in four sampling campaigns. The first two campaigns were conducted in the rainy season in August and September 2018 and the last two were in the dry season in March and April 2019 (season factor). In addition, the August and March campaigns were carried out during the ebb tide and the September and April campaigns were conducted during the flood tide (tide factor). For each of sampling sites from No. 2 to No. 12, two water samples per site were taken on the confluence of the Saigon River and its main tributaries (urban canals), one on the mainstream (the confluence) of the River (sample a, river position) and the other on the mouth (70–150 m far from the River, sample b) of the urban canal (canal position) (Fig. 1) (position factor). For sites No. 1 and No. 13, one water sample per site (sample a) was taken to examine input and output water quality for comparisons. Therefore, twenty-four water samples were taken in one sampling campaign (1 (site 1) + 11 (sites 2 to 12) × 2 (samples a and b) + 1 (site 13)), and ninety-six samples in total were taken in four campaigns for the current study.

Water sample collection and chemical analysis

On the day of sampling, a boat was used to travel from site 1 to site 13 depending on the tidal phase (ebb and flood) to take water samples for the 0–50 cm surface layer using a Van Dorn water sampler. For one sample, eight samplers distributed over the two sides of the River or canal mouth were taken into a 40-l bucket and finally around 5 l of water from this bucket was further taken into a plastic bottle with a firm cap, which was immediately stored in an ice-box at 4 °C and transported to a laboratory for analyses. In addition, water remaining in the bucket was measured directly for temperature, pH, electrical conductivity (EC), dissolved oxygen (DO), and turbidity using a thermometer, a pH meter, an EC meter, a portable DO meter, and a Hach DR/2010 spectrophotometer, respectively. The plastic bottle water samples were analyzed for eight heavy metal(loid)s, including Al, B, Bi, Fe, Mn, Pb, Sr, and Zn, following procedure by Giri and Singh (2013). In detail, the samples were filtered through Whatman No.42 filter paper into centrifuge tubes and the filtrate was acidified to pH < 2 using concentrated nitric acid, and then stored in a fridge at 4 °C until analysis. The concentrations of these metal(loid)s were measured using inductively coupled plasma-optical emission spectrometry (ICP-OES). The analysis was started with 8 standard solutions having different pre-known metal concentrations to establish a standard curve with a coefficient of determination of over 0.98. A calibration blank sample or a standard solution with a pre-known concentration was reanalyzed for every 15 samples to confirm the accuracy of the analysis.

Calculation and statistical analyses

The total concentration of the eight examined metal(loid)s (TCM) was computed by summing the measured concentration of these elements. For individual varimax factors from principal component analysis/factor analysis, the summative concentration of the metal(loid)s (SCM) was computed by summing the concentration of elements having high loading value with associated varimax factors. The concentrations of individual metal(loid)s and TCM were subjected to analysis of variance (ANOVA), based on a three-way model of three factors (the season, tide, and river position). A full statistical ANOVA model was $\gamma_{ijek} = \mu + \beta_i + \propto_j + \propto \beta_{ij} + \tau_e + \beta\tau_{ie} + \propto \tau_{je} + \alpha\beta\tau_{ije} + \varepsilon_{ijek}$, where γ_{ijke} is the response of the combination of three factors; μ is overall mean; β_i is a fixed effect of the *i*th season; α_j is the fixed effect of the *j*th tide; $\beta\alpha_{ij}$ is the interaction effect of season and tide; τ_e is the fixed effect of *e*th river position; $\beta\tau_{ie}$ is the interactive effect of season and river position; $\propto\tau_{je}$ is the interaction effect of tide and river position; $\alpha\beta\tau_{ije}$ is the interactive effect of season, tide, and river position; and $\in_{ijek}$ is the random error with mean zero and having normal distribution (Akhtar and Memon 2009). When the ANOVA result indicated a significant effect at $P \leq 0.05$, Tukey's honest significant difference test was used to classify treatment means.

Principal component analysis/factor analysis (PCA/FA) was conducted to apportion pollution sources and identify important heavy metal(loid) parameters. The PCA/FA was applied to each season to separate the pollution sources, following the procedure described by Eqani et al. (2011) and (Phung et al. 2015). Multiple regression analysis to quantify the contributive percentage of individual pollution sources (varimax factors) identified from PCA/FA to the TCM was carried out after doing the stepwise method to eliminate any uncorrelated factors and thus establish a final significant regression model (Putri et al. 2018). Pearson correlation matrix was conducted to examine the inter-relationship among the 8 metal(loid)s, helping to identify the pollution sources. Spatial variation of the TCM, SCM, and individual metal(loid) concentrations was examined using the scatter-graph method. All statistical analyses were conducted using JMP pro 13 (SAS Institute Inc., NC, USA) and all figures were established using Sigmaplot 12 (Systat Software Inc.).

Results

Selected properties of water and the status of heavy metal(loid)s

Although the eight examined heavy metal(loid)s and the total concentration of these elements were subjected to three-way ANOVA, only two experimental factors, season and tide were found to have a statistically significant influence on the elemental concentration. Consequently, the experimental factor of river position (river position and canal position) was not mentioned throughout the result and discussion section.

Eight heavy metal(loid)s of 96 surface water samples were analyzed and the summary results are shown in Table 1. In general, the total concentrations of the examined metal(loid)s (TCM) were higher in the dry season 1.78, 1.88, 1.41, and 1.39 than the rainy season, 0.99, 1.00, 1.06, and 1.09 (mg L^{-1}) of four combinations (ebb tide + canal, ebb tide + river, flood tide + canal, and flood tide + river), respectively. For individual elements, the highest concentration was found with Al (averaged 0.35 mg L^{-1}) and the lowest concentration was with Pb (averaged 0.01 mg L^{-1}). In addition, five selected physiochemical properties of water were analyzed and the mean results are also shown in Table 1. The temperature of the surface water varied from 29.9 in the river position collected during the ebb tide in the rainy season to 32 °C in the canal position collected during flood tide in the dry season. The pH of the river water varied from 6.4 to 7.3 units; DO varied from 2.0 to 3.8 (mg L^{-1}); EC was from 183 to 5141 (μS cm^{-1}), and turbidity was from 18.1 to 57 (NTU).

Figure 2a shows that the TCM was significantly affected by the interaction of the tide and season. In the rainy season, the TCM of the two tides (ebb tide (0.99) and flood tide (1.08 mg L^{-1})) was not significantly different from each other. Meanwhile, in the dry season, the TCM was significantly higher during the ebb tide (1.83) than during the flood tide (1.40 mg L^{-1}). Figure 2b also shows that TCMs of water samples collected in the dry season were located above those

Table 1 Mean concentration and standard error (SE) of 8 examined metal(loid)s (mg kg^{-1}) and selected water properties (temperature, pH, DO (dissolved oxygen), EC (electrical conductivity), and turbidity). *TCM*, total concentration of examined metal(loid)s

Parameter	Statistics	Rainy season				Dry season			
		Ebb tide		Flood tide		Ebb tide		Flood tide	
		Canal	River	Canal	River	Canal	River	Canal	River
Al	Mean	0.32	0.32	0.41	0.40	0.31	0.30	0.38	0.37
	SE	0.007	0.008	0.035	0.029	0.007	0.005	0.020	0.014
B	Mean	0.06	0.05	0.04	0.04	0.26	0.30	0.20	0.20
	SE	0.006	0.003	0.003	0.003	0.029	0.042	0.011	0.011
Bi	Mean	0.0687	0.0683	0.0689	0.0674	0.0720	0.0728	0.0743	0.0741
	SE	0.0004	0.0006	0.0010	0.0003	0.0004	0.0002	0.0003	0.0003
Fe	Mean	0.38	0.42	0.43	0.41	0.30	0.26	0.15	0.13
	SE	0.050	0.041	0.069	0.037	0.021	0.019	0.040	0.018
Mn	Mean	0.10	0.08	0.05	0.10	0.15	0.14	0.14	0.15
	SE	0.011	0.008	0.013	0.011	0.015	0.015	0.020	0.024
Pb	Mean	0.010	0.010	0.011	0.009	0.016	0.016	0.017	0.016
	SE	0.0002	0.0003	0.0016	0.0002	0.0001	0.0001	0.0011	0.0002
Sr	Mean	0.03	0.03	0.03	0.06	0.65	0.75	0.43	0.43
	SE	0.01	0.00	0.01	0.01	0.13	0.16	0.05	0.05
Zn	Mean	0.02	0.01	0.01	0.02	0.03	0.03	0.03	0.02
	SE	0.004	0.003	0.002	0.001	0.002	0.010	0.003	0.003
TCM	Mean	0.99	1.00	1.06	1.09	1.78	1.88	1.41	1.39
	SE	0.05	0.04	0.12	0.05	0.15	0.21	0.11	0.08
T (°C)	Mean	30.1	29.9	30.8	30.7	30.5	30.1	32.0	31.7
	SE	0.2	0.3	0.1	0.1	0.1	0.1	0.2	0.1
pH	Mean	7.1	7.1	7.3	7.2	6.5	6.4	6.9	6.9
	SE	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.1
DO (mg kg^{-1})	Mean	2.0	2.6	2.6	2.9	2.8	3.8	3.1	3.5
	SE	0.2	0.3	0.3	0.2	0.2	0.2	0.1	0.1
EC (μS cm^{-1})	Mean	312	183	306	730	4068	5141	2804	2475
	SE	31	15	41	230	694	819	427	267
Turbidity (NTU)	Mean	57.0	45.5	33.1	30.5	23.5	19.1	21.4	18.1
	SE	3.6	2.9	3.1	3.2	3.2	1.3	1.5	1.4

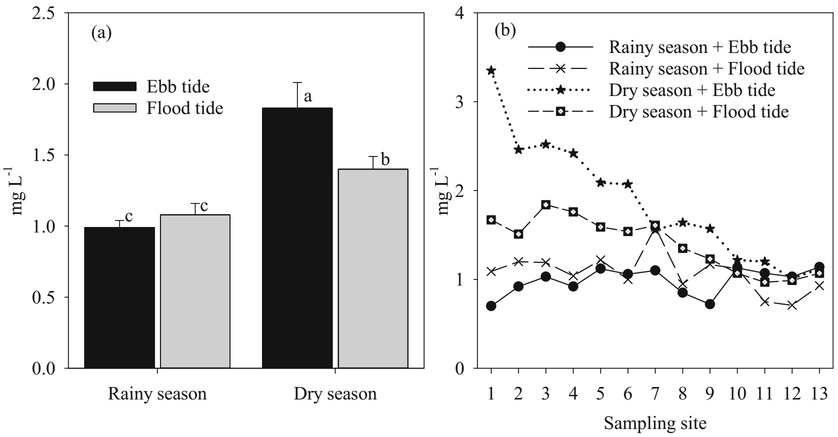


Fig. 2 The total concentration of examined metal(loid)s (TCM) (**a**) and spatial variation of the TCM (**b**) as affected by the interaction of tide and season. Within panel **a**, bars attached with the same letters are not significantly different from the other. Error bars indicate standard errors

collected in the rainy season. The TCM in the dry season, especially during the ebb tide, was decreased from site 1 to site 13 (from 3.35 to 1.12 mg L^{-1} for the ebb tide in the dry season, and from 1.67 to 1.07 mg L^{-1} for the flood tide in the dry season). For the higher sites (site 10 to site 13), the TCM of the four combinations tended to come closer to each other.

The two experimental factors, season and tide, had a significant interactive effect on the concentrations of B (Fig. 3 a and b), Sr (Fig. 3 c and d), Bi (Fig. 4 a and b), and Fe (Fig. 4 c and d). While in the rainy season, the B concentration was similar between the two tides, in the dry season the B concentration was significantly higher during the ebb tide (0.28) than during the flood tide (0.20 mg L^{-1}). The dynamics of the four combinations (rainy season + ebb tide, rainy season + flood tide, dry season + ebb tide, and dry season + flood tide) from site 1 to site 13 was a clearly decreasing pattern in the dry season but was a relatively flat model in the rainy season. For the last few sampling sites (sites 11–13), the B concentrations were still higher in the dry season than in the rainy season. The B concentration of four combinations of season and tide and in all 13 sampling sites was lower than the maximum permissible limit (MPL) or guideline standard of 2.4 (mg L^{-1}) by the World Health Organization (WHO). Similarly, the Sr concentration was not clearly different between the flood tide and ebb

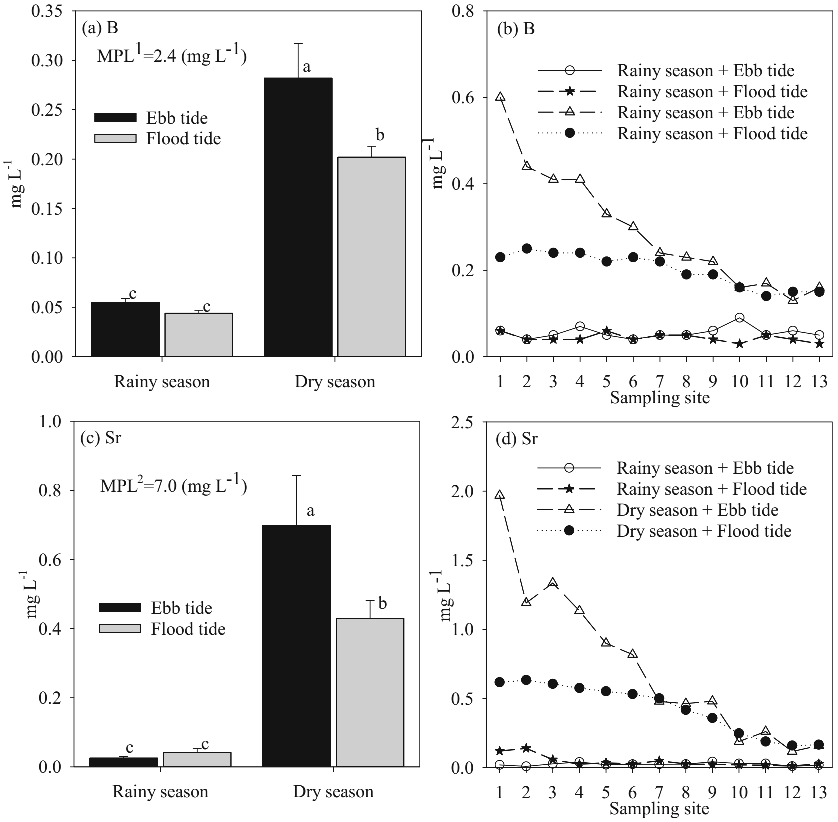


Fig. 3 The seasonal and spatial variation of B (**a** and **b**) and of Sr (**c** and **d**). Within a panel **a** or **c**, bars attached with the same letter were not significantly different from the other. Error bars indicated standard error. MPL^1 and MPL^2 = maximum permissible limit (standard) based on WHO (2017) and Health Canada (2018), respectively

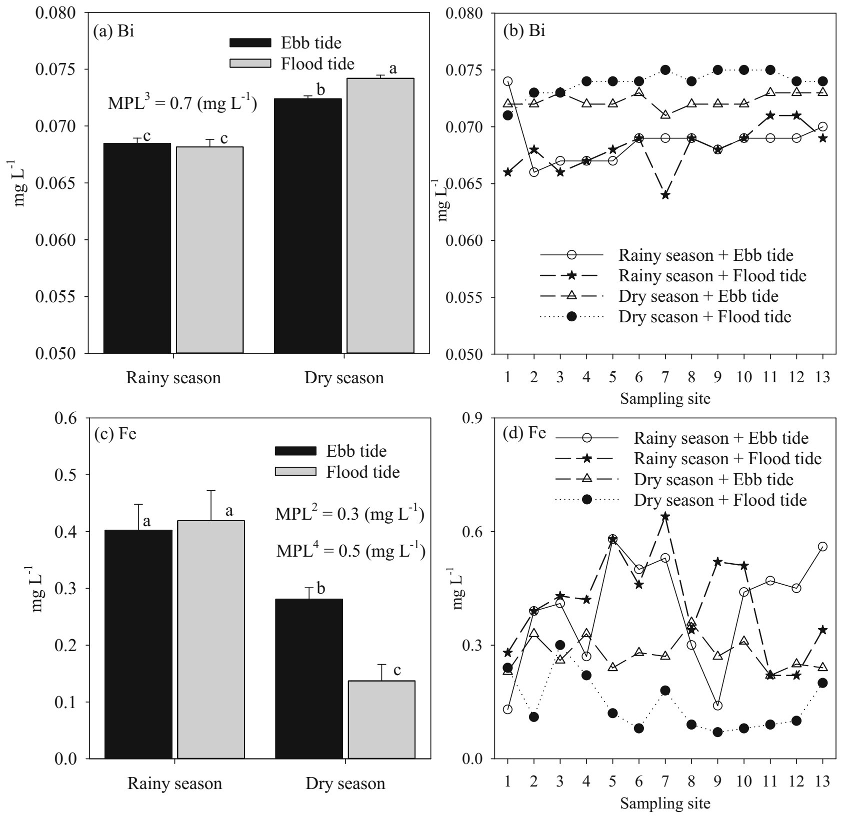


Fig. 4 The seasonal and spatial variation of Bi (**a** and **b**) and of Fe (**c** and **d**). Within a panel **a** or **c**, bars attached with the same letter were not significantly different from the other. Error bars indicated standard error. MPL^2, MPL^3, and MPL^4 = maximum permissible limit (standard) based on Health Canada (2018), ANZECC (2000), and MONRE (2015) respectively

tide in the rainy season but was significantly higher during the ebb tide than during the flood tide (Fig. 3 c and d) in the dry season. The dynamics of Sr concentration with sampling site was a decreasing pattern from site 1 to site 13 for the dry season, but relatively flat for the rainy season. The Sr concentration of all surface water samples collected from 13 sites was much lower than the Canadian standard by Health Canada.

The Bi concentration in the rainy season was similar between the ebb tide and flood tide (around 0.068 mg L^{-1}) but was significantly higher during the flood tide than during the ebb tide in the dry season (Fig. 4a). The spatial variation of the four combinations of the two experimental factors, season and tide, was a relatively flat pattern from the sampling site 1 to site 13 (Fig. 4b). The Bi concentration was much lower than the Australian and New Zealand standard (0.7 mg L^{-1}). The rainy season also had Fe concentration similar between the two tides (0.41 to 0.42 mg L^{-1}) but the dry season had Fe concentration significantly higher during the ebb tide (0.28) than during the flood tide (0.14, mg L^{-1}) (Fig. 4c). The Fe concentration of the four combinations tended to be higher in the sampling sites from 4 to 13 (Fig. 4d). From site 4 to site 13, Fe concentration during the flood tide in the dry season was lower than that of the other combinations. The averaged Fe concentration of four combinations was lower than the national standard (0.5 mg L^{-1}) by the Ministry of Natural Resources and Environment (MONRE) of Vietnam but that observed in the rainy season was higher than and that measured in the dry season was lower than the Canadian standard by Health Canada (0.3 mg L^{-1}).

The concentrations of Mn (Fig. 5 a and b), Pb (Fig. 5 c and d), and Zn (Fig. 6 a and b) were significantly affected by only season, higher in the dry season than in the rainy season, while the concentration of Al was significantly higher in the flood tide (0.39) than in the ebb tide (0.31 mg L^{-1}) (Fig. 6 c and d). In the dry season, the averaged concentration of Mn was 0.14, that of Pb was 0.016, and that of Zn was 0.70 significantly higher than those in the rainy season, 0.14, 0.01, and 0.03 mg L^{-1}, respectively. These concentrations varied with sampling sites depending on the elements, higher in the sites from 2 to 11 for Mn, relative flat for the Pb, and varying greatly site by site for Zn. The Al concentration dynamics was generally a decreasing pattern from sampling site 1 to site 13, except site 7 during the flood tide. The averaged Mn concentration in the dry season was higher than the Canadian standard and national standard (0.12 and 0.1 mg L^{-1}, respectively), while that in the rainy season was lower than the standards. The averaged concentration of Pb in both seasons was lower than the national standard by the MONRE (0.02 mg L^{-1}) but higher than the international standard by the WHO (0.01 mg L^{-1}). The averaged concentration of Zn in both seasons was lower than the Australian and New Zealand standard (0.03) and national standard (0.5 mg L^{-1}), while the averaged Al concentration was much higher than the international standard by WHO (0.2 mg L^{-1}).

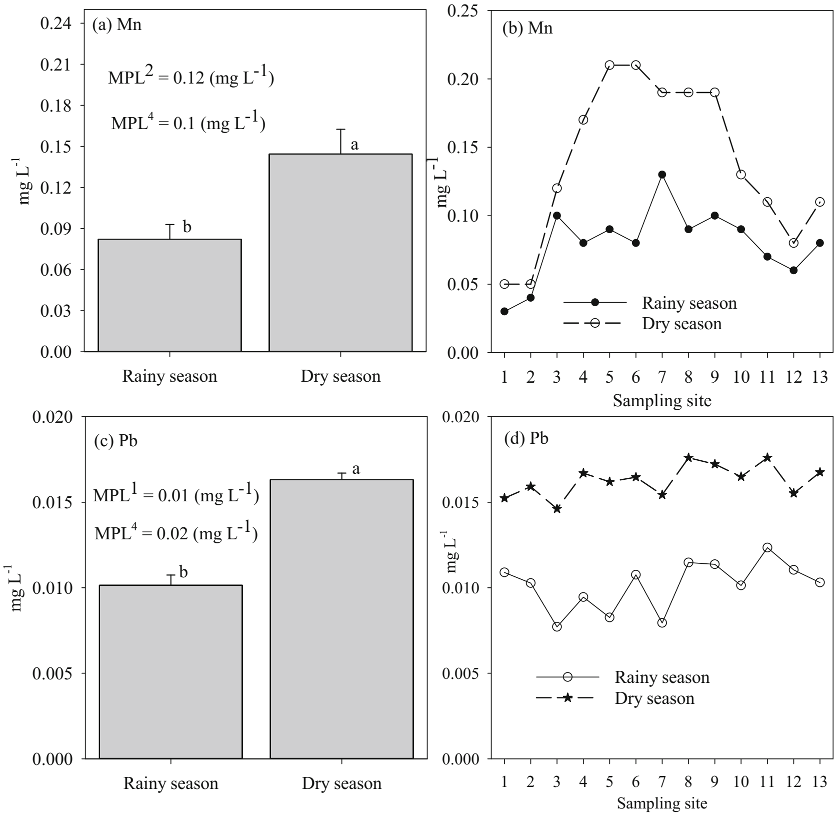


Fig. 5 The seasonal and spatial variation of Mn (**a** and **b**) and of Pb (**c** and **d**). Within a panel **a** or **c**, bars attached with the same letter were not significantly different from the other. Error bars indicated standard error. MPL^1, MPL^2, and MPL^4 = maximum permissible limit (standard) based on WHO (2017), Health Canada (2018), and MONRE (2015) respectively

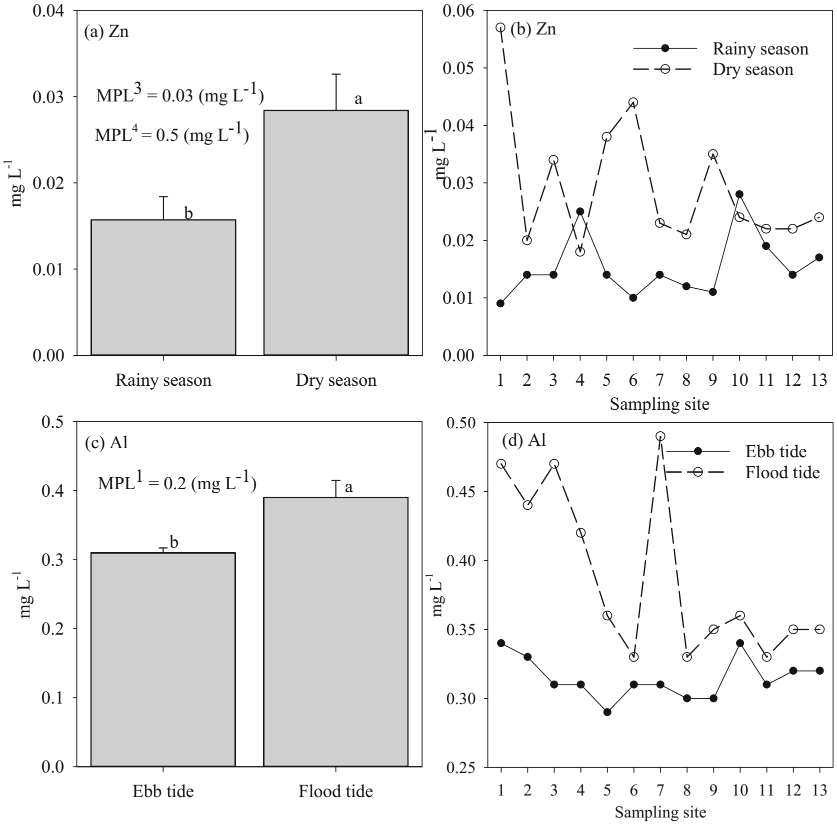


Fig. 6 The seasonal and spatial variation of Zn (**a** and **b**) and of Al (**c** and **d**). Within a panel **a** or **c**, bars attached with the same letter were not significantly different from the other. Error bars indicated standard error. MPL^1, MPL^3, and MPL^4 = maximum permissible limit (standard) based on WHO (2017), ANZECC (2000), and MONRE (2015) respectively

Results of multivariate analysis

Because the above section indicated that the concentrations of the 8 examined heavy metal(loid)s in surface water were significantly affected by the season, principal component analysis/factor analysis (PCA/FA) was applied on the rainy and dry seasons separately (Table 2). For both seasons, three varimax factors (having eigenvalue greater than 1) were extracted that together explained 69.7 and 68% of the total variance of the metal(loid) concentration in the rainy and dry seasons, respectively. For the rainy season, the varimax factor 1, explaining 36% of the total variance, was well correlated with Bi, Fe, Mn, and Pb (loading value greater than 0.5). The varimax factor 2 had high loading value with Al and Sr, and the varimax factor 3 had high loading with B and Zn. For the dry season, the most important varimax factor 1, explaining 34% of the total variance of total metal(loid) concentration, was correlated with B, Sr, and Zn, the factor 2 with Bi and Fe, and factor 3 with Al and Pb.

Correlation matrix analysis among the examined metal(loid)s showed that the Pearson correlation coefficients were significant among the metal(loid)s having strong loading values within individual varimax factors of each season (Table 3). For example, Bi, Fe, Mn, and Pb having high loading value with varimax factor 1 in the rainy season were significantly correlated with each other. Multiple regression analysis showed that for the rainy season, of the three factors, the first two factors were significantly correlated with the TCM (Table 4). Factor 1 explained 53% and factor 2 explained 16% of the total variance of the TCM in the rainy season. For the dry season, the three factors were significantly correlated with the TCM that explained 73, 12, and 3%, respectively (together explained 89%) of the total variance of the TCM.

The dynamics of three varimax factors

Based on three factors identified through PCA/FA, the concentrations of the metal(loid)s having high loading values with individual factors were summed up (summative concentration of metal(loid)s based on PCA, SCM) and examined using the scatter-graph method (Fig. 7). For factor 1 (VF1), the dynamics of the SCM in the rainy season was relatively flat, while that in the dry season was a rapidly decreasing pattern from site 1 to site 13 (Fig. 7a). For factor 2 (VF2), the SCM in the rainy and dry seasons varied greatly from site to site but tended to decrease from site 1 to site 13 and that in the dry season was lower than that in the rainy season (Fig. 7b). For factor 3 (VF3), the dynamics of the SCM in the rainy season were also relatively flat from site 1 to site 13 and that in the dry season was much greater than that in the rainy season (Fig. 7c).

Discussion

Heavy metal(loid) status and the effect of the season and tide

Overall, the concentration of the eight metal(loid)s in surface water collected from the Saigon River varied greatly with the season and tide. The significant interaction between the two factors determined the concentration of B, Sr, Bi, Fe, and finally TCM (Figs. 3, 4, and 2) respectively. In the rainy season, the concentration of Fe, Pb, and Al was higher than the international standards (0.3 mg L^{-1} for Fe, Health Canada 2018; 0.01 mg L^{-1} for Pb, WHO 2017; and 0.2 mg L^{-1} for Al, WHO 2017) (Figs. 4c, 5c, and 6c), while in the dry season,

Table 2 Loading values of 8 examined heavy metal(loid)s from principal component analysis/factor analysis. Bold numbers are those greater than 0.75, and italic numbers are those greater than 0.5 and smaller than 0.75

Parameter	Rainy season			Dry season		
	VF1	VF2	VF3	VF1	VF2	VF3
Al	− 0.23	**0.81**	− 0.20	− 0.23	0.17	**0.80**
B	0.08	− 0.16	**0.83**	**0.91**	− 0.27	0.11
Bi	**0.77**	− 0.43	− 0.08	− 0.06	**0.92**	0.02
Fe	*− 0.73*	0.02	− 0.21	0.12	**− 0.89**	0.14
Mn	*− 0.69*	− 0.17	0.43	− 0.13	0.03	− 0.47
Pb	**0.75**	− 0.24	− 0.15	− 0.08	0.31	*− 0.70*
Sr	− 0.02	**0.85**	0.17	**0.91**	− 0.20	0.12
Zn	− 0.22	0.32	*0.69*	*0.65*	0.12	− 0.08
Eigenvalue	2.87	1.52	1.19	2.69	1.54	1.24
% total variance	35.83	19.01	14.90	33.58	19.22	15.55
Cumulative percentage variance	35.83	54.84	69.74	33.58	52.80	68.35

Table 3 The Pearson correlation coefficients (*r*) among the 8 measured metal(loid)s

Parameter	Al	B	Bi	Fe	Mn	Pb	Sr	Zn
Rainy season								
Al	1.00							
B	− 0.18	1.00						
Bi	− 0.45*	0.06	1.00					
Fe	0.36*	− 0.07	− 0.41*	1.00				
Mn	− 0.06	0.23	− 0.47*	0.30*	1.00			
Pb	− 0.24	0.00	0.70*	− 0.32*	− 0.42*	1.00		
Sr	0.51*	− 0.02	− 0.39*	− 0.04	0.08	− 0.24	1.00	
Zn	0.20	0.34*	− 0.30*	0.13	0.29*	− 0.28*	0.23	1.00
Dry season								
Al	1.00							
B	− 0.14	1.00						
Bi	0.18	− 0.27	1.00					
Fe	0.03	0.37*	− 0.71*	1.00				
Mn	− 0.13	− 0.12	0.16	− 0.01	1.00			
Pb	− 0.28*	− 0.19	0.23	− 0.27	0.12	1		
Sr	− 0.12	0.96*	− 0.20	0.29*	− 0.11	− 0.18	1.00	
Zn	− 0.13	0.37*	− 0.03	0.02	− 0.03	− 0.02	0.35*	1.00

*The correlation coefficient was statistically significant at $p \leq 0.05$

the concentration of Bi, Mn, Pb, and Al was higher than these standards (0.7 mg L^{-1} for Bi, ANZECC 2000; 0.12 mg L^{-1} for Mn, Health Canada 2018; 0.01 mg L^{-1} for Pb, WHO 2017; and 0.2 mg L^{-1} for Al, WHO 2017) (Figs. 4a, 5a, c, and 6c), respectively. These indicated that water in the dry season could be more contaminated with metal(loid)s than that in the rainy season. Previously, Strady et al. (2017) concluded that the concentration of some trace metals such as As, Cd, Cr, Cu, Zn, and Hg in surface water of the same river was lower than the international standard by WHO and national standard. Some possibilities to explain these differences between the two studies could include (1) the river was more polluted since the study by Strady et al. (2017) and (2) the metal set measured in the two studies was different, except Zn, which was lower than the standards in both cases.

The interesting finding from the current study was the significantly interactive effect of season and tide on the TCM in surface water collected from the Saigon River. While the dry season had significantly higher TCM than the rainy season, the effect of the tide was significant in the dry season but insignificant in the rainy season (Fig. 2a). Other studies reported higher concentrations of metals in the dry season than in the rainy season (Aigberua 2017; Edokpayi et al. 2017). The mechanisms related to the finding could be involved in water evaporation and lower rainfall in the dry season, relative to the rainy season, increasing the metal(loid) concentrations.

Table 4 Percentage of individual varimax factors (VF) from PCA/FA in explaining the total variance of TCM (total concentration of examined metal(loid)s) in two seasons. Stepwise elimination was applied first and the multiple regression model describing the dependence of TCM on three VFs was finalized

Source	Rainy season			Dry season		
	Sum of squares	Percentage	Metal(loid)s**	Sum of squares	Percentage	Metal(loid)s
Factor 1	1.35	52.86*	Bi, Fe, Mn, Pb	9.95*	72.76	B, Sr, Zn
Factor 2	0.41	15.92*	Al, Sr	1.70*	12.40	Bi, Fe
Factor 3	0.01	0.25	B, Zn	0.35*	2.54	Al, Pb
Error	0.79	30.97		1.68	12.30	
Total variance	2.56	100.00		13.68	100.00	

*The factor was significant at $p \leq 0.05$

**These metal(loid)s used to compute the summative concentrations of metal(loid)s based on PCA (SCM)

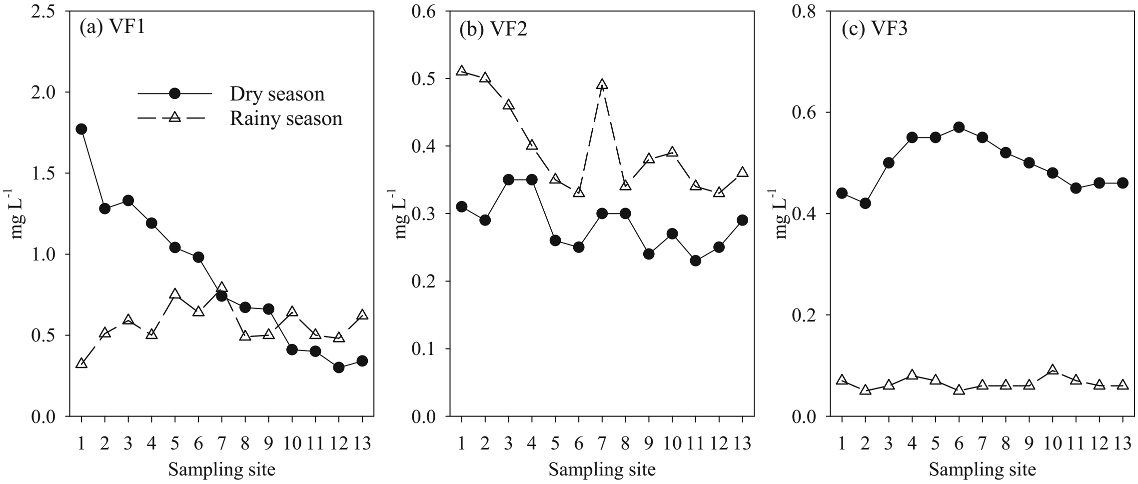


Fig. 7 Dynamics of summative concentration of metal(loid)s determined by PCA/FA (SCM) of the three varimax factors over the sampling sites (SCM was the sum of the concentration of metal(loid)s having high loading values with individual VFs as shown in Table 4)

Meanwhile, high rainfall during the rainy season may cause the dilution effect, which additionally reduced the TCM, relative to the dry season (Aigberua 2017). In addition, the flat pattern of sampling site-based variation of the TCM of water samples collected during the rainy season (Fig. 2b) may also indicate that the environments surrounding the examined river could be cleaner in the rainy season than in the dry season, reducing pollution sources from the inside of Ho Chi Minh City. In addition, EC of the dry season was much higher than that of the rainy season (Table 1), indicating that river water in the dry season was contaminated with inorganic cations than that in the rainy season, in agreement with the TCM higher in the dry than in the rainy season. In contrast, the river water in the rainy season was higher in turbidity and pH, while lower in DO than the dry season, indicating that the rainy season was more contaminated with organic substances than the dry season.

For the tidal effect, on average, a higher TCM observed during the ebb tide than during the flood tide may indicate that the outgoing tide could bring more pollutants from the river catchment or from inside Ho Chi Minh City to cumulatively add metal(loid)s to surface water along the river. The tidal effect on the water quality of a tidal river was reported by other studies. For example, Aslan et al. (2018) found that some water quality parameters such as dissolved oxygen (DO) and turbidity were higher during the flood tide than during the ebb tide. Sanderson and Taylor (2003) reported that some water parameters, such as total suspended solids (TSS), could reach their maximum values during the ebb tide that was due to erosion or drainage from surrounding canals and upper agricultural soils. Similarly, the current study found that turbidity and EC of water were higher and DO was lower during the ebb tide than during the flood tide (Table 1), indicating that the ebb tide may transport the organic and inorganic wastes and effluents from inside Ho Chi Minh City or upper catchment to the Saigon River.

During the rainy season, because high rainfall could regularly wash/carry the metal-containing materials such as agricultural, municipal, and industrial wastes out of the upper catchment and/or from the inside Ho Chi Minh City, the TCM in the examined-river water was low and not significantly affected by the tidal currents (ingoing and outgoing currents), making the TCM of river water similar between the two examined tides. In the meantime, during the dry season, the same effect of high rainfall could be limited, and thus the ebb tide may transport more metal-containing materials to examined-river water than the flood tide did.

For individual metal(loid)s, B and Sr behaved similarly to the TCM that could be explained with the above assumptions, while the others were slightly different from the general pattern of the TCM. Although being no interactively affected by the season and tide, the concentration of Mn, Pb, and Zn was significantly higher in the dry season than in the rainy season. Similar findings were also reported in other studies (Edokpayi et al. 2017), and the authors attributed the difference to the dilution effect during the rainy season and evaporative effect during the dry season. The significantly higher Al concentration during the flood tide than during the ebb tide could be explained with an intrusion of Al from lowland areas surrounding the River's estuarine area, such as the Can Gio mangrove forest and acid sulfate soil (Tran et al. 2019). For Bi, the dry season was also observed with a significantly higher Bi concentration than the rainy season that could be explained with dilution and evaporative effects (Edokpayi et al. 2017). Higher Fe concentration in the rainy season than in the dry season could be due to transport of the metal(loid) from acid sulfate soil from inside Ho Chi Minh City to the river that would be discussed in more detail in the following section.

Sources of the metal(loid)s

Sampling site-based variation of the TCM (Fig. 2b) showed that the sites from 10 to 13 were contaminated with metal(loid)s lesser than the other sites located on and/or close to the mouth of the Saigon River, typically the samples collected in the dry season and ebb tide. For these water samples, lower TCM in the upper sampling sites and higher TCM in the lower sampling sites suggested that the overall metal(loid)s could mainly originate from the inside Ho Chi Minh City or be resuspended from the bottom sediment of the lower sites due to much activity of cargo ships in the area. Principal component analysis/factor analysis revealed that the 8 examined metal(loid)s could be derived from three sources, which could be different between rainy and dry seasons. For the rainy season, the most important source, having high loading values with Bi, Fe, Mn, and Pb and explaining 36% of the total variance of the TCM (Table 2), could be derived from inside Ho Chi Minh City, because sites 2 to 12 had higher SCM than the 2 sites at the two ends had (Fig. 7a). The origin of Fe and Mn were also identified to come from the River's middle reaches, which released Fe and Mn from acid sulfate soils and from sediment through dissolution (Ha et al. 2011). The same sources of these four metals in the rainy season could be highly possible because they had significant correlation coefficients with each other (Table 3). The second source of metals having high loading value with Al and Sr in the rainy season could come from the lowland areas, which could be the mangrove forest and acid sulfate soils. The Saigon River is connected to a large mangrove forest of around 32,000 ha in Can Gio district (Miyagi et al. 2014). The mangrove forest is normally characterized by high aluminum concentration (Naidoo and Raiman 1982), which could be the case of the Can Gio Mangrove forest. Consequently, the flood tide brought Al to the river, forming a dynamics of Al over the sampling site (high concentration in sites 1 and 2 and low concentration in sites 12 and 13) as shown in Fig. 6d. The third source of metal(loid)s for B and Zn (varimax factor 3 in the rainy season) was unclear because the dynamics of SCM of the two metal(loid)s over the 13 sampling sites were a relatively flat pattern (Fig. 7c). One possibility for their origin could be from the atmosphere inputs (Aksu 2015; Rose-Koga et al. 2000) because the non-point source of pollution may distribute B and Zn quite equally over the sampling sites in the rainy season.

For the dry season, three pollution sources of the examined metal(loid)s were extracted from PCA/FA (Table 2). The most important source, associated with varimax factor 1 and represented by B, Sr, and Zn, could be derived from the lowland areas beyond the river estuary or from the brackish water, inferred from a gradual decrease of SCM from site 1 to site 13 (Fig. 7a). While a possible source of B and Zn could be from atmosphere in rainy season (above discussion), which additionally diluted their concentration, lowering their concentration in the rainy season than in the dry season (Figs. 3a and 6a), the possible source of B and Zn could be from the brackish water or seawater (Kabay et al. 2010; Neff 2002; Wolska and Bryjak 2013) in the dry season, which induced the evaporative effect, increasing the concentration of these metal(loid)s. In addition, as possibly originated from industrial and domestic wastes (Dong et al. 2012), Zn concentration was found to be higher in sampling sites 1, 3, 4, and 5 than the others (Fig. 6b), indicating that industrial and residential activities along the riverside areas in the lower reaches could be one of the main sources of the element in the dry season. The second source of the metal(loid)s, represented by Bi and Fe, could come from inside Ho Chi Minh City, but varying with point sources of pollution. Some sites such as 3, 4, 7, and 8 had SCM of Fe and Bi higher than the other sites, indicating that these sites could receive a considerable amount of Fe and Bi from either acid sulfate soil or industrial and domestic wastes (Ha et al. 2011; Kumar et al. 2017). The sources of Fe and Bi in the dry season were similar to those in the rainy season. The last source associated with varimax factor 3 for Al and Pb could originate from the middle sampling sites (sites 3–10), which had SCM higher than the other sites at the two ends had (Fig. 7c). For the rainy season, in addition to the dilution effect, high rainfall also induced surface runoff and/or disturbance of sediment in the mangrove forest, containing a high Al concentration (Andrade et al. 2018), that brought Al to the river, started from site 1 upon flood tide, as discussed above. For the dry season, these effects could be negligible in replacement of the runoff from acid sulfate soils from areas surrounding site 3 to site 10, increasing the Al concentration of these sites. The main source of Pb was still from inside Ho Chi Minh City, which was similar to that in the rainy season.

Contribution of different pollution sources

Overall, three pollution sources contributing to enriching the examined metal(loid)s in surface water of the Saigon river were identified and quantified that were different between the dry and rainy seasons (Table 4). The three main sources of metal(loid)s in the Saigon River were identified and could be grouped into two major origins, including anthropogenic activities from inside Ho Chi Minh City such as industrial and agricultural production as well as the discharge of domestic waste and natural processes in the lowland areas beyond the river estuary, such as acid sulfate and paddy soil, mangrove forest, and brackish water. As a megacity in Vietnam with the highest population and density and industrial zones and plants (Schneider et al. 2017), Ho Chi Minh City released a large amount of solid and liquid wastes to the environment daily, polluting Saigon river water. For example, Quynh and Ba (2003) pointed out that heavy metal(loid) sources in some soils in Ho Chi Minh City could be derived from industrial and household wastewaters. The Saigon River is affected by the semidiurnal tide regime from the East Sea of Vietnam that could bring some metal(loid)s to the river from the areas beyond the estuary, being important sources of metal(loid)s. Although the sources may not be changed from season to season, the rainy period may reduce the influences of the sources, while the dry period may strengthen their effects, altering the impacts of these pollution sources.

The pollution source from the upper catchment insignificantly contributed to the metal(loid) concentration in water of the river, although the catchment spread over a large area of 4717 km^2 (Lahens et al. 2018) over two main soil types, Ferralsols and Acrisol, which are characterized by low pH (Pham 2010). The soils had high concentrations of Al and Fe (Nguyen and Thai 1995), and thus, erosion and/or runoff over those soils may bring a great amount of the Al- and Fe-rich soil materials to the Saigon River, enriching these two metal(loid)s in water of the lower reaches of the River. Nevertheless, the current study revealed that such the hypothesis was unable to confirm as discussed above. The reason could be the natural self-purification of the river (Kuriata-Potasznik et al. 2016), that can be involved in several processes such as dilution, sedimentation, and adsorption of the dissolved metal(loid) ions and suspended-metal-carried materials. Because the self-purification needs a distance to remove the metal(loid)s from the liquid phase (Tian et al. 2011), point sources of pollutions located on the Saigon river banks or inside Ho Chi Minh City, or non-point sources of pollution from the lowland areas beyond the river estuary contributed mainly to enriching the examined metal(loid)s in the current study.

Conclusions

The current study revealed that overall the total concentration of 8 metal(loid)s (TCM), including Al, B, Bi, Fe, Mn, Pb, Sr, and Zn, was higher in the sites close to the estuary of the Saigon River than in the sites far from the river mouth in the dry season, but not in the rainy season. Moreover, while in the rainy season, the TCM in the two tides (ebb and flood tide) was not clearly different from each other, in the dry season, the TCM was significantly higher during the ebb tide than during the flood tide. Three main pollution sources of the metal(loid)s were identified, quantified, and grouped into anthropogenic activities such as industrial, agricultural production, and discharge of domestic wastes from inside Ho Chi Minh city, and natural origins such as lowland area and acid sulfate soil beyond the river estuary. The three pollutions sources together explained 70% and 68% of the total variance of the TCM in the rainy and dry seasons, respectively.

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