



Trace metals in aquatic environments of a mangrove ecosystem in Nansha, Guangzhou, South China: pollution status, sources, and ecological risk assessment

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Abstract Mangrove forests are widely located along coastlines. They have been identified to be inimitable and dynamic ecosystems. This study investigated the trace metals in mangrove water and surface sediments of Nansha, Guangzhou, China. Zn ($148.42 \pm 247.47 \mu\text{g L}^{-1}$) was the most abundant metal in waters, followed by As ($82.34 \pm 118.95 \mu\text{g L}^{-1}$), Pb ($22.96 \pm 120.50 \mu\text{g L}^{-1}$), and Ni ($19.42 \pm 47.84 \mu\text{g L}^{-1}$). In sediments, the most abundant metal was Fe ($27.04 \pm 1.91 \text{ g kg}^{-1}$), followed by Mn ($1049.04 \pm 364.11 \text{ mg kg}^{-1}$), Zn ($566.33 \pm 244.37 \text{ mg kg}^{-1}$), and Cr ($106.9 \pm 28.51 \text{ mg kg}^{-1}$). Higher contents of trace metals were detected in vicinity areas of the river mouth. The results of pollution indexes, including

contamination factor, enrichment factor, and geo-accumulation index, indicated the pollution of Cd, Cu, Pb, and Zn in sediments. The Spearman correlation and cluster analysis were used to evaluate the metal sources. In water, the significant correlations among Zn and water chemical parameters (Na, Mg, K, Ca, conductivity, pH, and Cl) might indicate the natural source of Zn from the seawater. Water sampling sites in estuaries and coastal areas were clustered separately, which might indicate the influences of upstream water and the seawater, respectively. In sediments, the significant relationships among Cd, Pb, and Zn concentrations were likely to imply the emissions from industries and exploitation of the Pb-Zn mine. The occurrence of Cr and Cu in sediments can be attributed to the spills of lubricants or oil. Cd in sediments could cause serious ecological risk.

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Introduction

The rapid urban development and the extensive industrial activities have led to numerous water environmental problems around the world (Chen et al. 2016; Zhang et al. 2017). Among them, the trace metal pollution in aquatic environments has attracted great concerns due to their toxicity and non-biodegradation (Liang et al. 2016). The mangrove grows along estuaries and intertidal zones of sub-tropical and tropical coasts (Wu et al. 2014). These mangrove ecosystems provide various

ecological services and sustain the integrity of coastal areas (Costa-Böddeker et al. 2017). Mangrove ecosystems are exposed to a variety of contaminants from domestic wastewater, industrial effluents, marine activities, and so on (Gil et al. 2011; Saha et al. 2006). The trace metal pollution in these ecosystems is predominantly caused by copper (Cu), zinc (Zn), manganese (Mn), cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) (Li et al. 2015; Liang et al. 2016). These metals are easily fixed, accumulated, transferred, and enriched in mangrove ecosystems, due to their physico-chemical properties as well as the high contents of clay and silt in the mangrove aquatic environment (Cline and Upchurch 1973; Lau and Chu 2000). For example, high concentrations of Cd were detected in the mangrove sediments in Futian, South China, which has been drawing high concern due to its adverse biological effects (Li et al. 2015). In addition, the clay and silt probably played an important role in raising the levels of Cr, Cu, and Zn (Li et al. 2015). Due to the rapid economic development along the coastal regions in China, the concerns on the trace metal pollution in mangrove ecosystems have been risen (Liu et al. 2017; Tao et al. 2005; Zhang et al. 2014). Plenty of studies have reported the serious pollution of trace metals in mangrove areas in South China (Liu et al. 2014; Tam and Yao 1998; Xu et al. 2015). Therefore, it is important to monitor and assess the levels, distributions, as well as ecological risks of trace metals in mangrove ecosystems.

In South China, mangroves are mainly distributed in the Pearl River Estuary (PRE) (Jin 2018). The Nansha mangrove (NM) is located in Nansha Distract, Guangzhou, and is one of the largest mangrove ecosystem in the PRE (Wu et al. 2015). The areas of NM increase steadily with the highest annual growth rate of 20.15% from 2010 to 2012 (Jin 2018). A previous study found a severe contamination of trace metals in surface sediments in NM, which might be attributed to the discharge of industrial sewage (Wu et al. 2014). However, no systematic research has been conducted on the metals in water and sediments in these mangroves. Pollution status, sources, occurrences, and spatial distributions of trace metals in NM water and sediments are still needed. Such data are important for understanding the mangrove function and the pollution levels. Therefore, this study aimed to (1) investigate the levels and distribution characteristics of trace metals in water and surface sediments of NM, (2) identify the potential sources, and (3) assess the ecological risk.

Materials and methods

Study area

Nansha (22°26'00" N-113°13'07.5" E to 23°06'15" N-113°43'07.5" E) is characterized with a subtropical monsoon climate. The mean annual temperature and precipitation were 22.2 °C and 1646.9 mm, respectively. In this study, the remote sensing and image interpretation (Giri et al. 2014) as well as in situ investigation were used to provide up-to date information about the species, quantities, and distributions of mangroves in the Nansha area. The supervised classification by maximum likelihood classifier (MLC) has been used to classify the satellite data from Landsat 8. Results showed that the Shanghengli Channel, Jiaoxi Dam, and Coastal Park were covered with mangroves with areas of 298,500, 88,600, and 138,600 m², respectively. A large area of farmland and residence were located along the Shanghengli Channel and the north side of Jiaoxia Dam. *Aegiceras corniculatum*s and *Sonneratia caseolaris* are the dominant mangrove species in the Shanghengli Channel. However, many mangrove species were grown in the Jiaoxi Dam and Coastal Park, including *Aegiceras corniculatum*s, *Sonneratia caseolaris*, *Acanthus ilicifolius*, and *Kandelia candel*s. These species are also dominant in wetland parks in Nansha (Jin 2018).

Sample collection and preparation

In March 2015, based on the distribution of mangroves in Nansha, ten sites were chosen in three major mangrove areas (Fig. 1): Shanghengli Channel (S1-S4), Jiaoxi Dam (S5-S6), and Coastal Park (S7-S10). The water samples were carried by polyethylene terephthalate bottles. Surface sediments (0–2 cm) were collected using a portable Ekman grab sampler during the low tide and sealed in polythene bags. Physico-chemical parameters including pH, conductivity, and temperature were simultaneously measured in situ using a calibrated multi-parameter probe (HQd, HACH, America). After collection, all samples were transferred to the lab within 1 day and stored in the dark under 4 °C until pretreatment. The water samples were filtered through hydrophilic fiberglass filter membranes (HFFMs, 0.5 µm, Shanghai Xingya purifying material factory, China) in laboratory. Then, 10-mL filter liquor was pipetted for analysis. Due to the limitation of sampling conditions and permission, only seven sediment samples at sites S3, S5 to S10 were collected (Fig. 1). The sediment samples

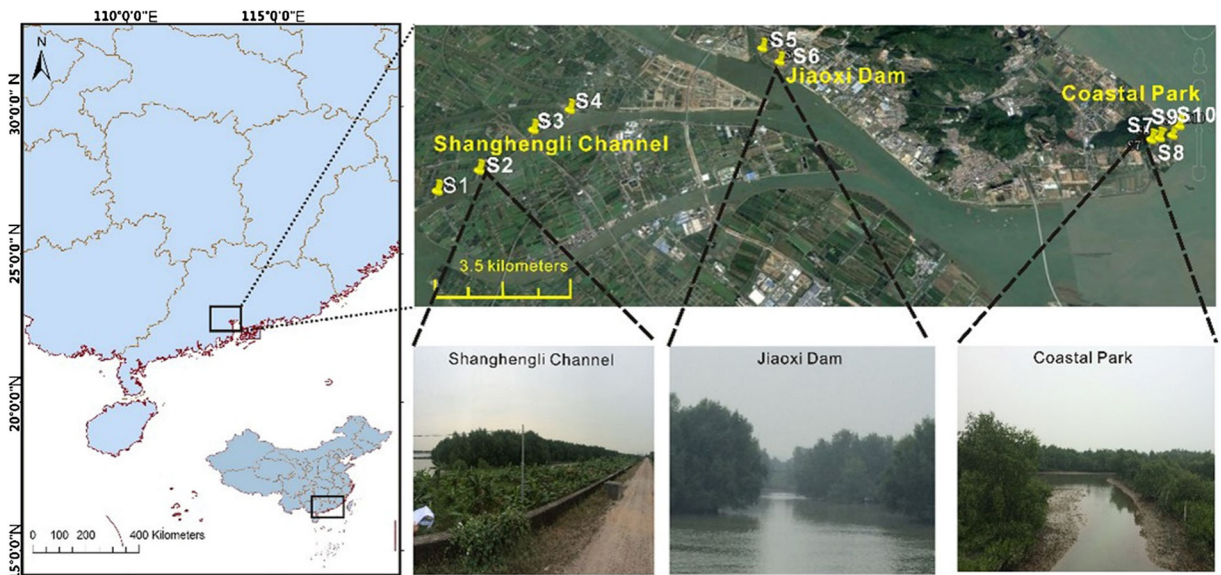


Fig. 1 Sample locations in NM

were air-dried, crushed, homogenized, and sieved through 75- μm mesh. Each sediment sample was weighed accurately (0.100 ± 0.001 g) and digested with 6-mL aqua regia (hydrochloric acid (V_{HCl})/nitrate acid (V_{HNO_3}) = 3:1) in a microwave digestion device (MARS-X, CEM, America). After cooling down to the room temperature (ca. 20 °C), the digestion solution was diluted to 100 mL with ultrapure water, then filtered through HFFMs (0.45 μm). Ten-milliliter digestion solution was pipetted for analysis.

Instrumental analysis and quality assurance

Trace metals (including Se, Fe, Mn, Cd, Pb, Cr, Cu, Zn, As, and Ni) and alkaline earth metals (including Na, Mg, K, and Ca) were analyzed by an inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher, America). The anion elements (including NO_2^- , NO_3^- , Cl^- , and SO_4^{2-}) were analyzed by an ion chromatograph (ICS-1000, Thermo Fisher, America). Quality control was carried during analysis. Trip blanks, consisting of ultrapure water, were taken into the field, and then taken back to the laboratory and analyzed. Acid blanks were used to determine the contamination from the acids and deionized water. Calibration curves were prepared for metals by appropriate dilution of certified standard stock solutions. The calibration curves with $r^2 > 0.999$ were accepted for concentration calculation. To assess the stability of the instrument and metal recoveries, a standard solution was analyzed after every five samples.

The quality control gave good precision for all the metals. The recoveries for all the metals ranged from 90 to 98%, and the relative standard deviation ranged from 2.21 to 5.18%. Concentrations were reported as the averages of triple measurements. The IBM SPSS Statistics software (Version 19.0) and Microsoft office software were used for data analysis. CorelDRAW X7 and OriginPro 2017 were used for graph drawing. Spearman correlation and cluster analysis were performed to show the relationships among elements and water qualities. Differences were statistically tested at the 5% significance level with one-way ANOVA test.

Results and discussion

Water chemical properties

The concentrations of conductivity, pH, alkaline earth metals, and anion elements in water samples are presented in Table S1 (Supporting Information). The pH values were slightly higher than 7.7, indicating a weakly alkaline environment. The values of conductivity, Na, Ca, K, Mg, Cl^- , and NO_2^- in Coastal Park water were significantly higher than those in upstream sites (ANOVA, $P < 0.05$). The highest conductivity was found in the Coastal Park water ($13,570 \mu\text{s cm}^{-1}$, Table 1), which was lower than that in seawater ($53,000 \mu\text{s cm}^{-1}$) (Castro et al. 2004). These results

Table 1 The concentrations of chemical parameters and major ions in water samples

Water chemical properties	Conductivity ($\mu\text{s cm}^{-1}$)	pH	Na (g L^{-1})	Mg	K	Ca	Cl ⁻ (mg L^{-1})	SO ₄ ²⁻	NO ₂ ⁻	NO ₃ ⁻
Shanghengli Channel	320.00 ± 7.07	7.73 ± 0.04	9.82 ± 3.11	6.57 ± 2.10	2.79 ± 0.92	37.67 ± 6.34	15.17 ± 1.39	32.16 ± 0.85	0.57 ± 0.77	6.79 ± 4.60
Jiaoxi Dam	908.00 ± 98.00	7.75 ± 0.07	59.55 ± 13.24	12.51 ± 2.21	4.94 ± 0.22	35.79 ± 3.54	17.19 ± 4.23	8.93 ± 0.82	ND	4.83 ± 2.27
Coastal Park	13,565.00 ± 4754.69	7.95 ± 0.12	1924.00 ± 683.52	276.97 ± 96.63	81.42 ± 27.17	131.36 ± 21.46	78.89 ± 47.20	27.74 ± 20.47	2.38 ± 1.43	1.55 ± 0.83
In all samples	5735.60 ± 7068.04	7.82 ± 0.14	785.30 ± 1025.3	115.90 ± 145.03	34.67 ± 41.87	74.76 ± 48.35	41.06 ± 43.01	25.75 ± 15.57	1.18 ± 1.43	4.30 ± 3.92
Trace metals	Cd ($\mu\text{g L}^{-1}$)	Pb	Cr	Cu	Zn	As	Ni	Se	Fe	Mn
Shanghengli Channel	0.08 ± 0.08	1.90 ± 1.31	0.98 ± 0.36	3.15 ± 0.56	4.55 ± 3.80	6.73 ± 1.58	0.43 ± 0.74	ND	10.10 ± 2.44	1.03 ± 0.13
Jiaoxi Dam	0.50 ± 0.50	6.00 ± 6.00	2.00 ± 2.00	2.00 ± 2.00	18.00 ± 2.00	44.50 ± 15.50	ND	17.00 ± 17.00	6.00 ± 2.00	3.50 ± 3.50
Coastal Park	6.88 ± 10.51	52.50 ± 90.93	11.25 ± 16.72	41.25 ± 42.19	357.50 ± 283.14	176.9 ± 140.99	48.13 ± 65.94	2.50 ± 4.33	7.50 ± 12.99	8.75 ± 8.93
Average	2.88 ± 7.41	22.96 ± 62.44	5.29 ± 11.69	18.16 ± 32.69	148.4 ± 247.47	82.34 ± 118.95	19.42 ± 47.84	4.40 ± 10.31	8.24 ± 8.56	4.61 ± 6.82
NSQS Class II	5.00	5.00	100.00	10.00	50.00	30.00	10.00	20.00	NA	NA
CV (%)	257	272	221	180	167	144	246	234	10	148

ND no data detected, NA no data available, CV coefficient variation

might indicate that the Coastal Park is a joint between the river and sea water (Sharma et al. 2007). The alkaline earth metals in NM water were in the order of $\text{Na} > \text{Mg} > \text{Ca} > \text{K}$, which is consistent with a previous research (Yan et al. 2010).

Trace metals in water

The concentrations of chemical parameters and major ions in water samples are shown in Table 1. The coefficients of variation (CV) of trace metals (144–272%) were higher than those in waters of a coastal zone in Southern Vietnam (14–152%) (as shown in Table 1) (Costa-Böddeker et al. 2017), suggesting a great variations of trace metal distribution in the study areas. Zn was the most abundant metal in waters, followed by As, Pb, and Ni (Table 1). The concentrations of Cd, Pb, Cr, Cu, Zn, As, and Ni in waters of Coastal Park were significantly higher than those in upstream (ANOVA, $p < 0.05$). The Coastal Park is located in the confluence area of the Humen Waterway and Jiaomen Waterway, in which the freshwater/seawater interaction is strong. At the freshwater/seawater interface, the ionic strength could be increased which leads to the redissolution of sediment-bound species (Huang et al. 1988). This could be the reasons for the higher levels of metals in the Coastal Park. This result is consistent with a previous study which showed that high concentrations of trace metals were observed in vicinity areas of river mouth (Gasparson and Burgess 2000). Furthermore, the highest concentrations of individual metals were all detected in sites collected from the Coastal Park.

Specifically, site S8 was detected with the highest concentrations of Fe ($30.00 \mu\text{g L}^{-1}$), Ni, ($160.00 \mu\text{g L}^{-1}$), Cu ($95.00 \mu\text{g L}^{-1}$), Zn ($820.00 \mu\text{g L}^{-1}$), As ($340.00 \mu\text{g L}^{-1}$), Cd ($25.00 \mu\text{g L}^{-1}$), and Pb ($210.00 \mu\text{g L}^{-1}$). The highest concentrations of Cr ($40.00 \mu\text{g L}^{-1}$) and Mn ($20.00 \mu\text{g L}^{-1}$) were found in sites S10 and S7, respectively. The aquaculture industry is developed in the Nansha area. Therefore, the National Seawater Quality Standard of China (NSQS) (class II) (GB 3097-1997) is used to assess the metal pollution herein. The average concentrations of Pb, Cu, Zn, As, and Ni were 3.59, 0.82, 1.97, 1.74, and 0.94 times higher than the corresponding threshold values shown in NSQS class II, respectively. The concentrations of trace metals in this study were higher than those observed in the PRE (Song 2014) and those detected in NM in 2013 (Xu et al. 2016), indicating a new discharge of trace metals into NM. Compared with other non-mangrove regions, the

concentrations of trace metals in this study were up to two orders of magnitude higher than those reported in Yellow River and Yangtze River, China (Zhang 2013), and Bahia Blanca estuary, Argentina (Botté et al. 2007) (Table S2, Supporting Information). The concentrations of Se in all sites (except site S6) were below the threshold, which might suggest the point input of Se in the water at site S6.

Trace metals in surface sediments

In sediments, the most abundant metal was Fe, followed by Mn, Zn, Cr, Pb, Cu, Ni, Cd, and As (Table 2). This composition was similar to that in mangrove sediments in Futian, China, which found that Zn, Cr, Pb, and Cu were predominant (Li et al. 2015). The order of trace metal concentrations was different with that observed in water samples in this study, which could be attributed to the different sediment/water partition coefficients between different trace metals (Hassan et al. 2010). The Gibbs free energy values of trace metals were ranked as $Cd^{2+} > Pb^{2+} > Cu^{2+} > Zn^{2+}$ (Zhuang and Shi 2003), which were consistent with the sediment/water partition coefficients of Cd, Pb, Cu, and Zn. These results indicated that Zn^{2+} was the most easily accumulated metal in sediments from water, followed by Cu^{2+} , Pb^{2+} , and Cd^{2+} (Zhuang and Shi 2003). Furthermore, the Zn concentrations in sediments were higher than other trace metals (except Fe and Mn). These jointly led to the high residual of Zn in sediments. However, the mean concentration of Pb was higher than Cu in sediments, which might relate to the high content of Pb in water (Table S1) and the high background level of Pb in sediments of PRE (Ma et al. 2014). The CV values in sediments ranged from 7 to 183%, which were much lower than those in water, indicating that the spatial variation was not as significant as those in water. These results could be explained by two reasons. Firstly, the intertidal water is more motivated than sediments. Secondly, the water is likely to be directly influenced by the coastal sewage discharge (Cao et al. 2006). The highest concentrations of Cd (11.45 mg kg^{-1}), Pb ($133.59 \text{ mg kg}^{-1}$), Zn ($957.06 \text{ mg kg}^{-1}$), and Ni (66.79 mg kg^{-1}) were observed at site S8 in Costal Park. This result was similar with those observed in waters in this study, which reflect that Cd, Pb, Zn, and Ni in water can deposit into the sediments (Thuong et al. 2015). The concentrations of Cr (69.09 mg kg^{-1}), Cu (6.46 mg kg^{-1}), and Ni (11.43 mg kg^{-1}) at site S10 were much lower than those in other sites, which might be attributed to the higher contents of coarse sand in sediments. Site S10 is

located in mudflat with coarse sediments; thus, the adsorption capacity of trace metals here is weak (Costa-Böddeker et al. 2017).

According to the functional division, values in the China Marine Sediment Quality Standard (CMSQS) (class I) (GB18668-2002) (Table 2) were used as the thresholds. The As concentrations were below the threshold, while the average concentrations of Cd, Pb, Cr, Cu, and Zn were 14.18, 1.43, 1.34, 2.30, and 3.78 times higher than the corresponding thresholds, respectively. These results suggested that the main pollutant in sediments was Cd, followed by Zn, Cu, Pb, and Cr. The results in our study were consistent with the results of a national survey of trace metals in China, which suggested that the Cd pollution was the most serious in the Guangzhou reaches of the Pearl River (China 2005). The trace metals above the corresponding thresholds in sediments were not exactly same with those in water.

Compared with other studies, Cd in the sediments of the study area was 10.74 to 141.80 times higher than non-mangrove regions in Coastal Bohai Bay, Northwestern Gulf of Thailand, the Yangtze River (Table S3, Supporting Information), and was 2.36 times higher than other mangrove regions that received industrial and municipal sewage (Tam and Yao 1998) (Table 2). Zn concentrations in sediments of the study area were 1.24 to 46.69 times higher than it was in non-mangrove regions in Coastal Bohai Bay, Northwestern Gulf of Thailand, the Yangtze River, and so on (Table S3), and was 2.36 times higher than other mangrove region that received industrial and municipal activity sewage (Tam and Yao 1998) (Table 2). In the Nansha area, the Cd concentrations in sediments (avg. 2.88 mg kg^{-1}) detected herein were slightly lower than those detected in 2008 (avg. 6.97 mg kg^{-1}) (Hu et al. 2011), but higher than those detected in 2012 (0.78 mg kg^{-1}) (Wu et al. 2014). The concentrations of Pb, Cr, Cu, and Ni were in the same level with other mangrove regions (Table S3). The higher concentrations of trace metals in Nansha mangrove might be due to the high level of local economic development to some extent (Sundaramanickam et al. 2016).

The enrichment degrees of trace metals (i.e., Cd, Pb, Cr, Cu, Zn, As, and Ni) in sediments were assessed by the following three numerical factors: contamination factor (CF) (Hakanson 1980), enrichment factor (EF) (Sinex and Wright 1988), and geo-accumulation index (I_{geo}) (Muller 1969).

$$CF = \frac{Me_s}{Me_b} \quad (1)$$

$$EF = \frac{(Me/Fe)_s}{(Me/Fe)_b} \quad (2)$$

$$I_{geo} = \log_2 \left(\frac{Me_s}{1.5Me_b} \right) \quad (3)$$

where Me_s refers to the metal concentration in the sediment sample and Me_b refers to the background value. $(Me/Fe)_s$ and $(Me/Fe)_b$ are the concentration ratios of the target metal to Fe in the sample and the background areas, respectively. Concentrations of Pb (21.90 mg kg^{-1}), Cr (69.30 mg kg^{-1}), Cu (16.10 mg kg^{-1}), Zn (94.30 mg kg^{-1}), and Ni (30.30 mg kg^{-1}) in the sediments of PRE were used as background values (Ma et al. 2014) (Table 2). The geochemical background values of Fe, Cd, and As ($20,240.00$, 0.30 , and 13.00 mg kg^{-1} , respectively) were used herein (Li et al. 2014) (Table 2), due to the absence of local background values. To reduce the variability associated with grain size, the EF method normalizes the metal contents with Fe as the reference metal, as these elements like Fe are not expected to be enriched from anthropogenic sources due to their relatively high natural concentrations (Sinex and Wright 1988).

Figure 2 shows the CF, EF, and I_{geo} values calculated from metal concentrations in sediments in the Nansha area. According to the CF values (Fig. 2), the contaminations of (1) Cd; (2) Pb, Cu, and Zn; (3) Cr and Ni; and (4) As were in the very high ($CF > 6$), high ($6 \geq CF > 3$), moderate ($2 \geq CF > 1$), and no pollution levels ($1 \geq CF > 0$), respectively. EF values of Cr and As were lower than 1.5, which suggested that Cr and As are mainly originated from parent materials and associated with natural processes such as the weathering of rock and soil (Li et al. 2009; Zhao et al. 2014). The I_{geo} values of Cd suggested that sediments in sites S3, S6, and S8 were strongly to extremely polluted ($5 \geq I_{geo} > 4$). As for sites S7, S9, and S10 were strongly polluted ($4 \geq I_{geo} > 3$). The I_{geo} values indicated uncontaminated to moderately contaminated of Pb, Cu, and Zn. The I_{geo} values were generally below zero for Cr, As, and Ni, which could be identified as the sampling sites were not polluted by them. In conclusion, Cd pollution was the most serious in sediments, followed by Cu, Pb, and Zn. Previous

research also showed that the exchangeable state of Cd content in the sediments of the PRE was high, which suggested that Cd in sediments at NM is easy to be redissolved and might pollute water environment (Yang and Zhang 2012).

Source analysis

In this section, the Spearman correlation and cluster analysis were used to diagnose the potential sources of metals in the water and sediments. In water, we observed significant correlations among Zn and water chemical parameters (including Na, Mg, K, Ca, conductivity, pH, and Cl) ($r^2 > 0.6$, $p < 0.05$). The variation of Na, Mg, K, and Ca contents indicated that the sampling water contained seawater (Sharma et al. 2007). Therefore, this result we found might indicate that Zn was originated from the seawater. Pb significantly correlated with Fe ($r^2 = 0.700$, $p < 0.05$), indicating that Pb and Fe might have similar source. This result differed with a previous study in the Pearl River, which showed a similar spatial distribution of Fe and Cu (Huang et al. 2012). Weak correlations ($|r^2| < 0.614$, $p > 0.05$) among Se, Mn, Cd, Pb, Cr, Cu, Zn, As, and Ni were obtained, indicating that these metals have different source, which could be related to the diverse anthropogenic activities (Wu et al. 2014). Cluster analysis through dendrogram was developed to understand the relationship between the metals at different sampling locations. As shown in Fig. 3, water sites were clustered to two major classes. Cluster A1 included sites S1 to S6, which are all located in the upstream areas. This result showed that sites S1 to S6 shared the same source of metals in water from the upstream areas. Cluster A2 included sites S7 to S10. These sites were greatly influenced by the seawater with higher concentrations of trace metals. This might indicate that metals in sites S7 to S10 were likely to originate from the seawater.

In sediments, Zn significantly correlated with Pb ($r^2 = 0.964$, $p < 0.01$) and Cd ($r^2 = 0.857$, $p < 0.01$), suggesting that these metals could be derived from the same source. Guangdong Province has the biggest reserve of the Pb-Zn mine compared with other provinces in China. Pb-Zn mines are mainly located in the upstream area of the Pearl River watershed (Liu and Qin 2016). Furthermore, high levels of Cd, Pb, and Zn have been detected in the Pearl River (Wu et al. 2014). Therefore, Pb, Zn, and Cd in the sediments of the study area were likely derived from the exploitations of Pb-Zn mines in the upstream areas

Table 2 The concentrations (mg kg⁻¹) of trace metals in sediments

Areas	Se	Fe	Mn	Cd	Pb	Cr	Cu	Zn	As	Ni
Shanghengli Channel	5.70	27,338.40	653.04	7.60	67.49	88.40	20.91	577.00	ND	31.37
Jiaoxi Dam	ND	28,124.75 ± 1954.93	1450.10 ± 0.10	7.15 ± 4.17	78.72 ± 44.86	122.21 ± 22.21	125.98 ± 18.44	419.65 ± 247.34	1.42 ± 1.42	67.90 ± 15.12
Coastal Park	4.18 ± 7.25	26,426.48 ± 1867.14	947.51 ± 319.49	6.94 ± 2.81	94.16 ± 36.59	103.87 ± 31.05	72.54 ± 41.58	637.01 ± 241.11	1.35 ± 1.46	38.99 ± 19.60
In all samples	3.21 ± 5.86	27,041.97 ± 1909.99	1049.04 ± 364.11	7.09 ± 3.08	85.94 ± 37.97	106.90 ± 28.51	80.44 ± 47.11	566.33 ± 244.37	1.17 ± 1.42	46.17 ± 21.92
GB18668-2002 class I	NA	NA	NA	0.50	60.00	80.00	35.00	150.00	20.00	NA
Background value	NA	20,240.00	NA	0.30	21.90	69.30	16.10	94.30	13.00	30.30
CV (%)	183	7	35	43	44	27	59	43	121	47

ND no data detected, NA no data available, CV coefficient variation

(Protano et al. 2014). Significant correlation between Cr and Cu in sediments ($r^2 = 0.929$, $p < 0.01$) was found. Generally, Cu has been used in lubricants (Fu et al. 2014). Oil spill was also found to be remarkably increased in the concentrations of Cu in marine sediments (Andersen et al. 2008; Andrade et al. 2004). Therefore, Cr and Cu in sediments in this study might originate from the lubricants or oil spill. Cluster analysis showed that sediment sites have different sources or properties (Fig. S1, Supporting Information). Marine current is also an influencing factor on metal accumulation in sediments (Ennouri et al. 2010).

Potential ecological risk assessment

Based on the principle of sedimentology, the potential ecological risk index (RI) (Hakanson 1980) is used to evaluate the potential risk of trace metals in the sediments herein. The concentrations, toxicity level, multi-factor synergism, and common rules of the transport and transformation of trace metals in sediments are taken into consideration. The RI values for total metals in sediments were calculated by the equation below:

$$RI_j = \sum_{i=1}^n E_j^i = \sum_{i=1}^n (T^i \times C_j^i) = \sum_{i=1}^n \left(T^i \times \frac{c_j^i}{c_r^i} \right) \quad (4)$$

where RI_j is the multi-heavy metal RI in sample j ; E_j^i is the single-heavy metal potential ecological risk index in sample j ; T^i is the toxic-response factor of the heavy metal i ($T^{Cd} = 30$, $T^{As} = 10$, $T^{Cu} = T^{Ni} = T^{Pb} = 5$, $T^{Cr} = 2$, $T^{Zn} = 1$). C_j^i is the pollution index of heavy metal i ; c_j^i is the measured concentration of the heavy metal i in the sample j ; c_r^i is the control value (background value) of heavy metal i . Background values used in the assessment have been mentioned above (Table 2). The levels and potential ecological risk indices are shown in Table 3.

The average potential ecological risk indexes (E_j^i) of individual metals in sediments were ranked as Cd (709.4) > Cu (25.0) > Pb (19.6) > Ni (7.6) > Zn (6.0) > Cr (3.1) > As (0.9). The exceptional high average E_j^i value of Cd (709.4) indicated a very high risk to the local ecosystem. The E_j^i values of the rest metals were all below 40. The average (standard deviation) RI of metals in sediments were 771.6 (299.9), with a range of 366.3 to 1228.5. Furthermore, all sites (except for site S5) had the RI values higher than 320. These jointly implied an extremely high risk of metal to the mangrove ecosystem in the Nansha area.

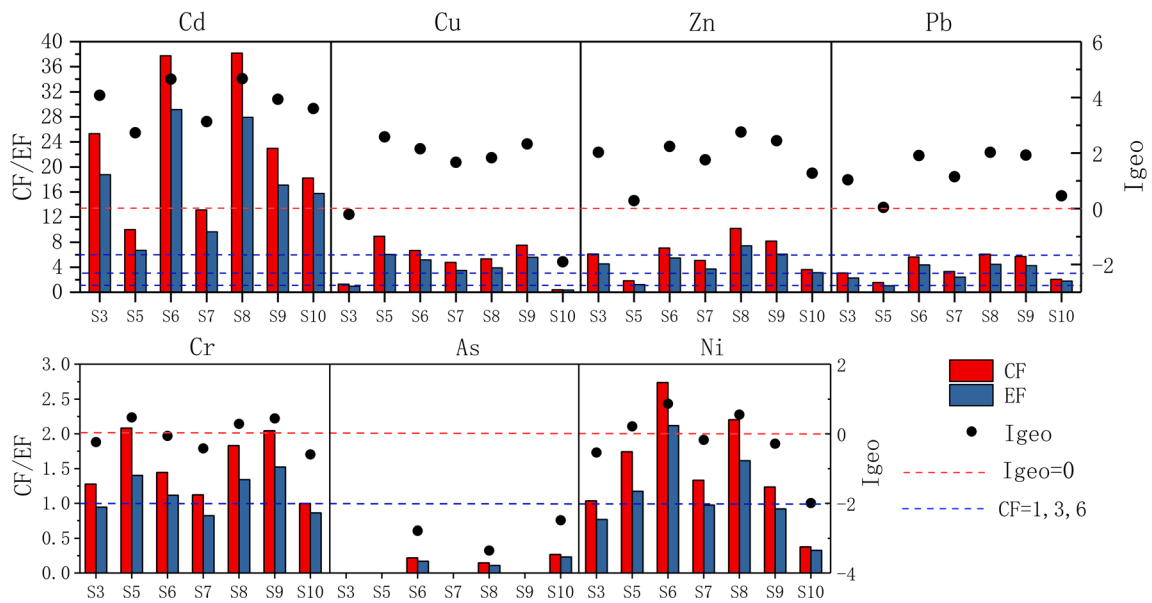


Fig. 2 CF, EF, I_{geo} based on environmental background values of trace metals in the NM

Conclusion

Zn was the highest abundant metal in waters, followed by As, Pb, and Ni. The result showed the higher concentrations of trace metals in vicinity areas of river mouth. The metals were impacted by anthropogenic activities especially for Pb, Cu, Zn, As, and Ni. In sediments, the most abundant metal was Fe, followed by Mn, Zn, and Cr. The deposition characteristic and the high concentration of Zn in water jointly led to the high residual of Zn in mangrove sediments. The lower CV values of trace metals in sediments than those in water samples, indicating that the trace metals in sediments showed less difference of geographical distribution. These results could be explained by two reasons. One is that the intertidal water is more motivated than sediments. Another is that the water is likely to be directly influenced by the coastal sewage discharge. Cd and Zn concentrations in sediments of the study area were

higher than non-mangrove regions and other mangrove regions that received industrial and municipal wastewater. The values of EF, CF, and I_{geo} show that Cd pollution was the most serious one in sediments, followed by Cu, Pb, and Zn. In water, the high correlation coefficients among Zn and water chemical parameters indicated that Zn has natural source. Cluster analysis showed that sites S1 to S6 which are located in the upstream areas shared the same source of metals in water and sites S7 to S10 were greatly influenced by the seawater with higher concentrations of trace metals. Correlation analysis shows that Pb, Zn, and Cd in sediments were likely derived from the exploitations of Pb-Zn mines in the upstream areas, while Cr and Cu in sediments might originated from the lubricants or oil spill. The extremely high potential ecological risk in sediments is mainly caused by Cd in study areas. The results of this research would be helpful to better understand the sources and toxicities of trace metals in water

Fig. 3 Cluster analysis dendrogram indicating the sample relatedness in water

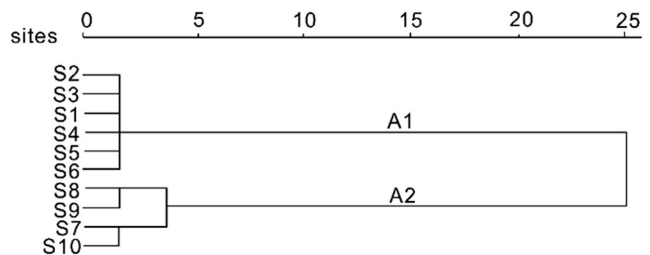


Table 3 Levels and potential ecological risk indices (ER and RI) (Hakanson 1980)

Ecological risk (E_j^i)	Potential ecological risk index (RI)
$E_j^i < 40$: low potential ecological risk	$RI < 150$: low ecological risk
$40 \leq E_j^i < 80$: moderate potential ecological risk	$150 \leq RI < 300$: moderate ecological risk
$80 \leq E_j^i < 160$: considerable potential ecological risk	$300 \leq RI < 600$: considerable ecological risk
$160 \leq E_j^i < 320$: high potential ecological risk	$RI > 600$: very high ecological risk
$E_j^i > 320$: very high potential ecological risk	

and sediments of Nansha mangrove and would provide significant information in heavy metal pollution control and human health protection.

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