Research papers

Occurrences of dissolved trace metals (Cu, Cd, and Mn) in the Pearl River Estuary (China), a large river-groundwater-estuary system

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A B S T R A C T

This study for the first time examined dissolved metals (Cu, Cd, and Mn) together with dissolved oxygen and carbonate system in the whole Pearl River Estuary system, from the upper rivers to the groundwater discharges until the estuarine zone, and explored their potential impacts in the adjacent northern South China Sea (SCS) during May–August 2009. This river-groundwater-estuary system was generally characterized by low dissolved metal levels as a whole, whilst subject to severe perturbations locally. In particular, higher dissolved Cu and Cd occurred in the North River (as high as 60 nmol/L of Cu and 0.99 nmol/L of Cd), as a result of an anthropogenic source from mining activities there. Dissolved Cu levels were elevated in the upper estuary near the city of Guangzhou (Cu: ~40 nmol/L), which could be attributable to sewage and industrial effluent discharges there. Elevated dissolved metal levels (Cu: ~20–40 nmol/L; Cd: ~0.2–0.8 nmol/L) also occurred in the groundwaters and parts of the middle and lower estuaries, which could be attributable to a series of geochemical reactions, e.g., chloride-induced desorption from the suspended sediments, oxidation of metal sulfides, and the partial dissolution of minerals. The high river discharge during our sampling period (May–August 2009) significantly diluted anthropogenic signals in the estuarine mixing zone. Of particular note was the high river discharge (which may reach 18.5 times as high as in the dry season) that transported anthropogenic signals (as indicated by dissolved Cu and Cd) into the adjacent shelf waters of the northern SCS, and might have led to the usually high phytoplankton productivity there (chlorophyll-a value > 10 µg/L).

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1. Introduction

A number of trace metals such as Fe, Cu, Cd, and Mn form enzyme co-factors or part of these co-factors in marine phytoplankton (Morel et al., 1991). Lack of these metals can limit algal growth in the ocean, whereas high levels may cause toxic effects (e.g., Bruland et al., 1991). Terrestrial inputs mainly from river runoff and submarine groundwater discharges (SGDs) deliver a substantial amount of nutrients and trace metals into the ocean, and so fundamentally influence their biological systems (e.g., Moore, 2006). Before being finally discharged into the ocean, these constituents are also subject to a series of geochemical reactions in estuaries, groundwaters and coastal waters, such as redox speciation changes (Turner et al., 1981; Wang and Sañudo-Wilhelmy, 2009), organic/inorganic complexation (e.g., Bruland and Lohan, 2003), particle desorption/adsorption (e.g., Roy et al., 2011), and precipitation/remobilization (e.g., Aller, 1990; Wang et al., 2011).

Human perturbations have long been recognized in small river estuary systems and especially in those urban waters. Once receiving substantial amounts of anthropogenic pollutants, these small water bodies commonly suffered eutrophication, and even periodic algal blooms and hypoxia locally, for example, the East River-Long Island Sound (e.g., Buck et al., 2005; Sañudo-Wilhelmy, 1999), the San Diego Bay and San Francisco Bay (Flegal and Sañudo-Wilhelmy, 1993), and the Po-Adriatic Sea system (Danovaro, 2003). However, the effects of human perturbations on these small systems are temporary and variable, and so they have a limited influence on coastal systems. Recent studies revealed that long-term anthropogenic impacts also occur in coastal waters, e.g., extended hypoxia (Diaz and Rosenberg, 2008), enhanced tidal intrusions (e.g., Robinson et al., 2007), and altered groundwater composition (Moore, 2006). Large rivers in relatively "pristine" zones contain relatively low levels of nutrients and metals, e.g., the Amazon (DeMaster et al., 1996), the Ob and the Yenisey (Dai and Martin, 1995), and therefore, these rivers have limited impacts on the coastal waters. In contrast, those large rivers with intensified human activities may be more representative in reflecting human impacts on a global scale. Heavily perturbed large rivers discharge high

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loadings of nutrients and contaminants into coastal waters, which may trigger coastal algal blooms on a large scale, e.g., the Mississippi (Justic et al., 2002), and the Yangtze (Zhang et al., 1999).

In addition to riverine discharges, chemical fluxes through groundwater discharges have recently been recognized as having a significant impact on coastal environments (e.g., Moore, 2006). Geochemical processes in the subterranean estuary may also modify the chemical composition in the SGDs, e.g., particle dissolution and metal sulfide oxidation, Mn oxide reduction and precipitation (Roy et al., 2011).

With the rapid economic development in China during the past several decades, the extensive use of chemical fertilizers and increasing domestic waste drainage through watersheds has resulted in increased fluxes and yields of nutrients into the ocean (Zhang, 1996). However, only a few widespread dissolved metal measurements are available for Chinese rivers, groundwaters, estuaries and marginal seas: e.g., in the Yellow and Yangtze Rivers (Zhang, 1995); in the Pearl River (Qu and Yan, 1990); in the Hong Kong waters (e.g., Cheung et al., 2003); in the Shenzhen groundwaters (Chen et al., 2007); and in the oligotrophic South China Sea (Wen et al., 2006). Gaillardet et al. (2003) also listed in the world river database some dissolved metal data for the Yellow and Yangtze Rivers. However, as far as the authors know, no systematic measurements have been done regarding dissolved metals in any single whole river-groundwater-estuary system in China so far.

2. Methods and materials

2.1. Study area

The Pearl River (PR) is the 13th largest in the world (2nd in China) with an annual average water discharge of $\sim 330 \times 10^9 \, \text{m}^3$, but with more than 70% occurring from May to August (PRWRC/PRRCC, 1991). The Pearl River Delta is fed by three major tributaries, namely the West (-72% of the water discharge), the North (-14%) and the East (-9%). These rivers, together with a series of smaller ones, discharge freshwater to the South China Sea (SCS) via three sub-estuaries: the Lingdingyang Bay, the Modaomen Outlet, and the Huangmaohai Bay. It is estimated that 50–55% of the PR freshwater is discharged into the Lingdingyang Bay (PRWRC/PRRCC, 1991), which is traditionally known as the Pearl River Estuary (PRE). The PRE is relatively deep in the central water channel (20–30 m), but shallow (< 5 m) along both sides with numerous mud flats or sandbanks (Fig. 1).

The PR Delta is one of the most industrialized zones in the world, and is surrounded by several huge metropolitan cities such as Guangzhou, Hong Kong and Shenzhen as well as many rural townships. Several scientific research projects have already showed increased loadings of contaminants in this river estuary system, e.g., the PRE Pollution Project (Chen et al., 2004). Obviously, the mega-metropolitan city of Guangzhou and other industrialized cities such as Dongguan significantly impact the upper estuary through sewage and industrial effluent discharges (Brigden et al., 2009). Consequently, dissolved oxygen (DO) dropped significantly from 113 μmol/L in 1990 to 30 μmol/L or lower over the last 20 years in the upper estuary (Zhai et al., 2005; Dai et al., 2006; Chen et al., 2008). Besides this, the discharged wastewaters from these places generally showed extremely high concentrations of dissolved metals (Brigden et al., 2009), which were expected to have effects in both the groundwaters and the estuary.

An extremely high river discharge (as high as $\sim 37 \times 10^3 \, \text{m}^3/\text{s}$ in the West River, ~ 18.5 times as high as in the dry season)

occurred during our sampling period in May–August 2009 (Fig. 2), which can be categorized as a "Medium to Large" flood according to the standard of Huang et al. (2004), and a historically low salinity was observed in the lower estuary (< 6). These settings provided us with an ideal place for studying anthropogenic influences on the rivers, aquifers, estuaries, and even the adjacent shelf waters.

### 2.2. Sampling location and sample collections

Water samples were taken in the whole PRE system, from the upper rivers to the groundwater discharges, until the coastline and estuarine waters in May–July 2009, and in the northern SCS in August 2009 (Fig. 1). Water samples in the upper rivers were taken at four hydrostations (Gaoyao, Shijiao, Boluo, and Tianhe). The groundwater samples were pumped out of wells along the coastline after purging 3 times the well volume. All the groundwater sampling sites are located in the Pearl River Delta near the cities of Shenzhen, Zhuhai, and Dongguan, and most of the wells were no longer used by humans long before our investigation. Coastline water samples were taken in the estuary, and these water samples were directly collected by using a precleaned plastic bucket with a rope 3 m away from the land. These sampling sites were less than 2 m in depth, and characterized by tidal intrusion, sediment resuspension, and groundwater seepages.

The estuary is divided into three sections according to their geomorphology and geochemical characteristics (Fig. 1): the upper estuary, which is characterized by a narrow and deep navigation channel, receiving a small fraction of freshwater from the north and East rivers, and also sewage and industrial effluent discharges from the cities of Guangzhou and Dongguan; the middle estuary, which basically refers to the inner Lingdingyang Bay with two shallow shoals and one deep navigation channel, receiving 53% of the freshwater from the North and West rivers with little salinity stratification; and the lower estuary, which refers to the outer Lingdingyang Bay with two wide shoals and two deep navigation channels, and is controlled mainly by estuarine mixing of the freshwater and seawater. Accordingly, the contrasting geochemical characteristics are listed in the Table 1. Estuarine water samples were collected from the whole estuary aboard a small wooden boat using Teflon tubing extended 3 m to one side of the boat into the surface waters (2–3 m deep) and connected to a low-flow peristaltic pump.

Adjacent shelf waters in the northern SCS were sampled during August 2009 aboard the R/V Dongfanghong-2 using an underway towed surface sampling system (modified from Vink et al., 2000). Samples were taken along a transect from outside the PRE to the continental shelf in the northern SCS (Fig. 1). Basically, a towed weight (coated with epoxy resin) with an intake was extended 6.0 m outside the wake of the vessel at a depth of approximately 2–3 m below the sea surface, and seawater samples were then pumped through Teflon tubing directly into a clean van on board. With surface anticyclonic circulation occurring in the shelf waters of the northern SCS (e.g., Wyrtki, 1961), a sharp salinity gradient clearly occurred between the lower estuary (salinity: ~ 6–12) and the shelf (salinity: ~ 31–34) as observed in this study.

2.3. Analytical methods

Salinity, temperature, pH, and DO were directly measured using either a WTW analyzer or a multiparameter sonde (YSI 6600). Filtered (0.45 μm) samples were analyzed for total alkalinity (Alk is used throughout) using an automated Gran titration analyzer with a precision of 0.1%, and dissolved inorganic carbon
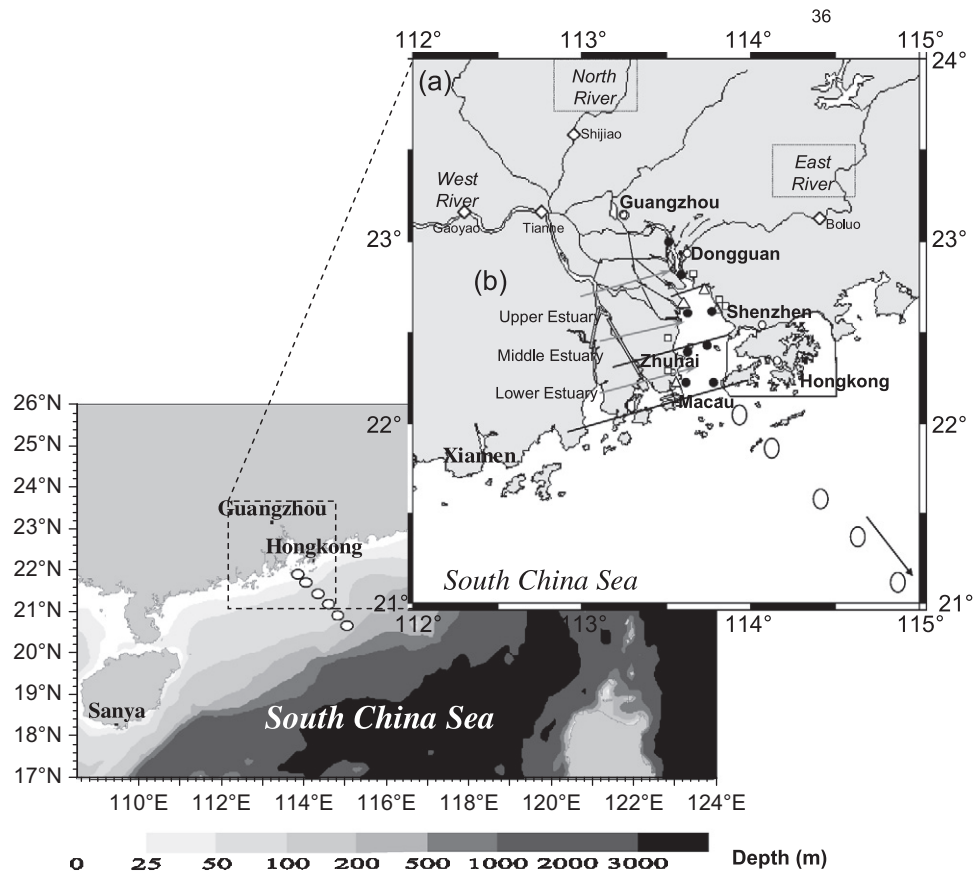
Fig. 1. Sampling stations in the Pearl River Estuary (right panel), and the northern South China Sea (NSCS) (left panel). Note: Upper Rivers (◇); Groundwaters (□); Coastline Waters (△); Estuarine Waters (●), and sampling locations (○stations of 9 to 2) in the NSCS.
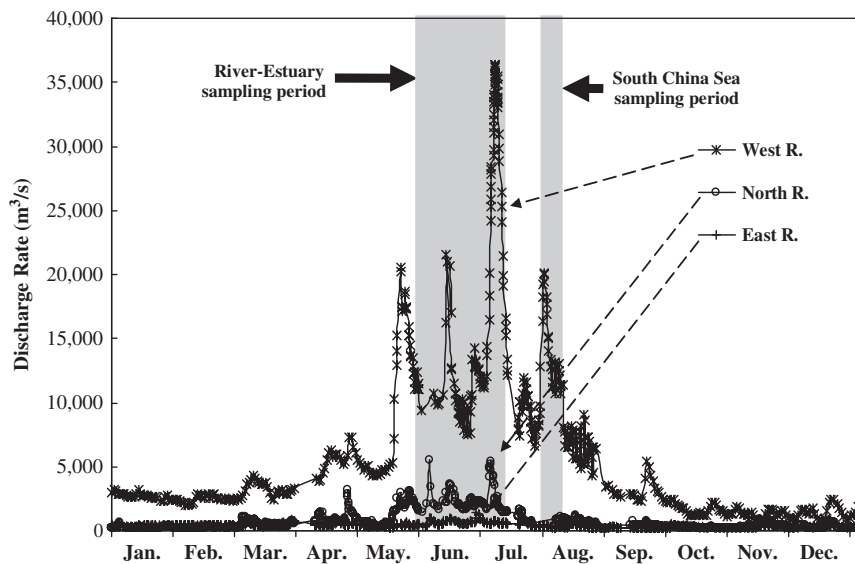
Fig. 2. Freshwater discharge rates in 2009 from the Gaoyao and Wuzhou hydrostations (the West River, the largest tributary contributing to ~72% of the total freshwater discharge of the Pearl River into the South China Sea, China Bureau of Hydrology, Ministry of Water Resources, http://sqqx.hydroinfo.gov.cn/websq/). The gray bar on the left indicates the sampling period for the river-groundwater-estuary system, and the one on the right for the South China Sea.

(DIC) with a nondispersive infrared CO_2 analyzer with a precision of 0.1% (Cai et al., 2004). Chlorophyll-a was measured for the shelf water samples following the method of Parsons et al. (1984). Basically, water samples were filtered under a pressure of less than 50 kPa, and extracted for 24 h in 90% acetone in 0 °C, and the fluorescent values were finally measured in a Hitachi 850 Fluorospectrometer.

All the metal samples were pumped on site using a peristaltic pump through an acid-washed 0.22 μm polypropylene calyx capsule filter, and collected into acid-cleaned 0.5 L HDPE bottles. The samples were then acidified to pH < 2 with 6 N HNO_3 (Fluka Ultra) and stored for at least a month until analysis. These acidified samples were preconcentrated with Chelex-100 resin followed by acid extraction (modified from Pai, 1988). Generally,

Table 1
Characteristics of salinity, DO, TA and DIC, dissolved Cd, Cu and Mn in groundwaters and surface waters from the estuary (upper, middle and lower) in the Pearl River Estuary system.

	Salinity	DO (μmol/L)	TA (mmol/L)	DIC (mmol/L)	Cd (nmol/L)	Mn (nmol/L)	Cu (nmol/L)
Groundwaters	0–0.3	20–180	0.86–4.64	2.09–5.96	0.11–0.21	5.4–1590	7–17
Estuary (coastline + estuarine)							
Upper	0	30–75	1.11–1.93	1.30–2.30	0.09–0.24	750–1480	24–38
Middle	0–5.3	100–170	1.3–1.95	1.42–1.49	0.12–0.39	5.3–1660	20–43
Lower	2.6–11.3	130–230	1.4–1.88	1.43–1.83	0.26–0.81	2.1–770	16–24

water samples were readjusted to pH 5.5 using ammonium acetate buffer, and then loaded onto the 2.0 g of Chelex 100 resin packed in the Poly-Prep columns (100–200 mesh, Bio-Rad Laboratories), and adsorbed metal ions were finally eluted with 1.0 N HNO_3 for ICP-MS (Agillent 7700) measurements. All the preconcentration and extraction procedures were conducted in a clean hood (class-100), and all tips, tubes, and bottles associated with the sampling, handling and sample water storage were acid-washed using cleaning protocols. The detection limits were estimated by three times of the standard deviation of triplicate procedural blanks as 0.009 nmol/L for Cd, 0.08 nmol/L for Cu and 0.06 nmol/L for Mn respectively. The accuracy of metal determination was checked with the certified reference materials (river water SLRS-4 and coastal water CASS-4) with less than 5% deviation for all measured metals.

3. Results and discussion

Over the past several decades, a series of environmental protection acts were applied in the PRE watershed, and, as a result, the water quality has been greatly improved especially in the PR, which serves as the most precious freshwater source supporting the densely populated Pearl River Delta including the cities of Guangzhou, Dongguan, Shenzhen, and Hong Kong. Anthropogenic perturbations under geochemically dynamic settings still provided an increased environmental pressure in the estuary (e.g., Brigden et al., 2009). Here, for the first time we observed occurrences of elevated dissolved metal levels (e.g., Cu, Cd, and Mn) in the whole estuary. Below we present the geochemical characteristics of water quality (e.g., inorganic carbon and dissolved oxygen), followed by dissolved metal distributions under anthropogenic influences in the estuary. Finally, the potential impacts of anthropogenic signals for coastal waters, especially in the adjacent shelf waters of the northern SCS, are discussed. In this study, dissolved metal levels (Cu, Cd, and Mn) are mainly used as indictors for defining the intensity and extent of anthropogenic perturbations.

3.1. Geochemical characteristics in the Pearl River Estuary

3.1.1. Total alkalinity and inorganic carbon

Alk and DIC in large rivers are mainly dictated by the chemical composition of rocks and the degree of carbonate weathering in the watershed (Cai, 2003). The West River (main stream) had a relatively high Alk (1.8–2.0 mM) since carbonate rocks are abundant in its drainage basin, but sparse in the East and North River basins (as indicated by low Alk values: 0.62 and 1.52 mM, respectively) (e.g., Chen and He, 1999).

Compared with these earlier data, our results showed slightly lower Alk: the West River, 1.68 mM; the East River, 0.56 mM; and the North River, 1.29 mM respectively (Fig. 3), which might have been attributable to the dilution effect during our high river discharge sampling period. In particular, a historic decrease of alkalinity in the West River is also likely to be related to
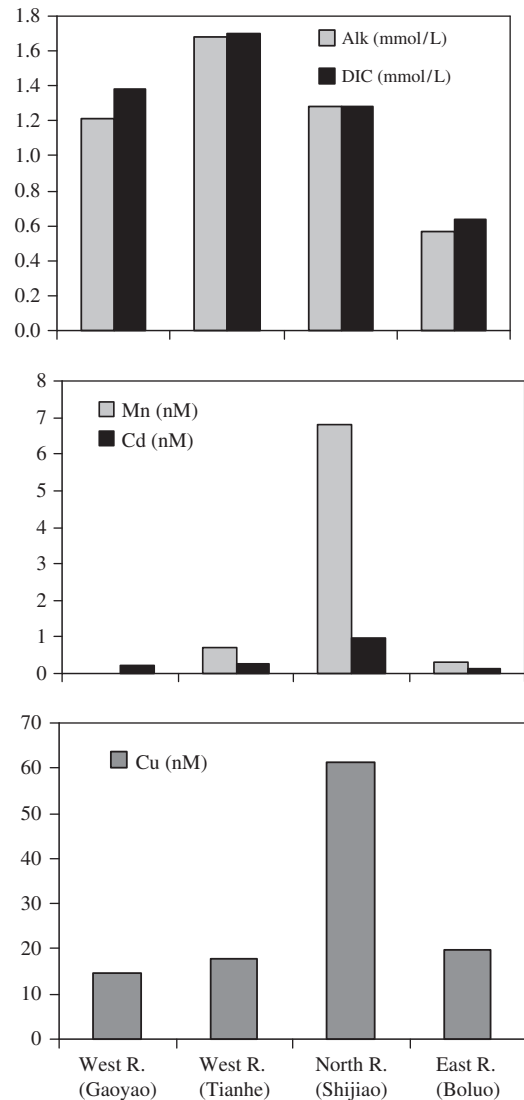

Fig. 3. The right panel shows the variations of Alk, DIC, dissolved Mn, Cd and Cu in the West, North, and East Rivers.

acidification due to industrial activities in recent decades (Chen and He, 1999; Zhang and Chen, 2002).

The groundwaters had a large variability in the DIC and Alk values (range, DIC: 2.09–5.96 mmol/L; Alk: 0.86–4.64 mmol/L, Table 1). The positively linear relationships of DIC and Alk against salinity in the groundwaters (Fig. 4) suggested that DIC and Alk were released progressively along the groundwater flowpath, which could be attributable to gradually enhanced organic matter decomposition in aquifers (e.g., Kessler, 1999), and the partial dissolution of calcite/aragonite (e.g., Cai et al., 2003). As a result, relatively high DIC and Alk (DIC: 1.83 mmol/L; Alk: 1.88 mmol/L; salinity: 11.3) were formed in the coastal waters near the city of
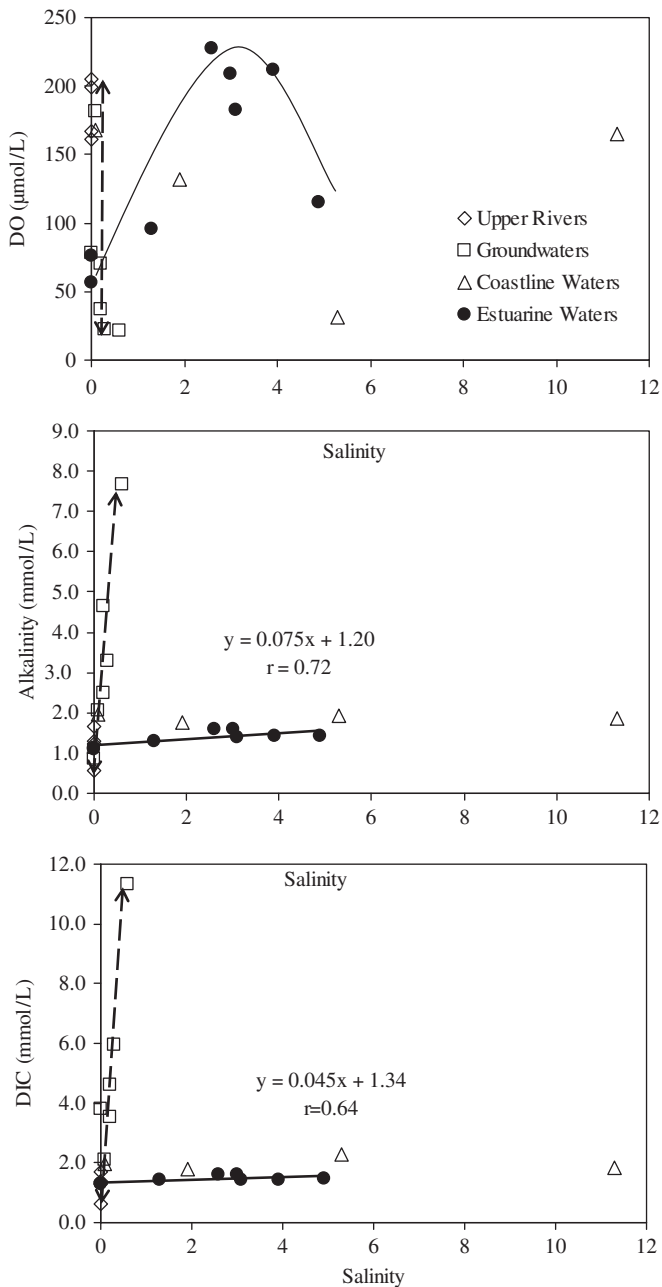
Fig. 4. Total alkalinity (Alk), DIC and dissolved oxygen (DO) vs salinity in the Pearl River Estuary system. The dashed lines indicate the near-zero-salinity endmembers: groundwaters (high Alk and DIC), and upper rivers (low Alk and DIC). The solid lines represent the linear fittings of Alk and DIC against salinity in the estuarine waters.

Zhuhai (Fig. 4), as influenced by recirculated seawater in sedimentary seepages.

In contrast to the groundwaters, the estuarine mixing zone was characterized by relatively less variable of DIC and Alk (DIC: 1.30–2.30 mmol/L; Alk: 1.11–1.93 mmol/L, Table 1). Positively linear relationships of DIC and Alk with salinity (Alk=0.075*Sal+1.20, $r=0.73$; DIC=0.045*Sal+1.35, $r=0.65$) occurred for the estuarine waters (Fig. 4), which indicated of estuarine mixing of freshwater (with its low inorganic carbon) and seawater (with its high inorganic carbon) as a dominant process in the estuarine waters, with little net biological uptake or release.

The values derived from extending the estuarine mixing straight line back to zero salinity are the effective values of

alkalinity (Alk*=1.20 mM) and DIC (DIC*=1.35 mM), which are also similar to the values previously reported in the estuary (e.g., Cai et al., 2004; Zhai et al., 2005; Guo et al., 2008). The relevance of the direct groundwater and river inputs into the estuary was estimated by using the effective concentrations of DIC* and Alk*, and, as a result, the groundwater discharge was calculated as accounting for ~7–9% of the total freshwater input in the estuary.

3.1.2. Dissolved oxygen

High levels of DO (160–205 μmol/L) were observed in the upper river waters (the hydrostations at Gaoyao, Shijiao, Tianhe and Boluo, Table 1), since these waters were highly dynamic with rapid water flow. However, low DO (30–75 μmol/L) occurred in the upper estuary near the industrialized metropolitan city of Guangzhou, which was mainly attributable to local discharges of sewage and industrial effluents. Such low oxygen waters in the upper reach of the PRE are also reported previously (Zhai et al., 2005; Dai et al., 2006; Chen et al., 2008).

Oxygen depletion was also observed in the groundwaters (as low as 20 μmol/L O₂) and the coastline waters (as low as 30 μmol/L O₂) (Fig. 4). Both groundwater and coastline water sampling sites were located within the Pearl River Delta, and surrounded by the cities of Guangzhou, Dongguan, Shenzhen, Zhuhai, and Macao, and so oxygen consumption occurred in the groundwaters, which has been attributable to organic matter decomposition along with the SGD flow (e.g., Roy et al., 2011). The low, but slightly increased, oxygen levels in the coastline waters mainly resulted from the atmospheric exposure of the reduced groundwater at the interface between groundwater and seawater.

In contrast to oxygen consumption in the "polluted" upper estuary, the middle estuary was characterized by the high levels of DO (100–170 μmol/L, Table 1), since it receives a substantial amount of the oxygenated freshwater from the upper rivers, and a series of hydrologic processes (e.g., wave and wind pumping, and density driven mixing, Martin et al., 2007) there also favors oxygen penetration from the atmosphere.

The lower estuary was characterized with high levels of DO (130–230 μmol/L, Table 1), although slightly low levels of DO observed in the shallow shoals near the city of Zhuhai (~130 μmol/L O₂), which was likely resulted from porewater seepages due to the SGDs (e.g., Roy et al., 2011). Generally, these water bodies were mixed with oxygenated SCS seawaters along with the flow path, and saturated or over-saturated oxygen (>205 μmol/L) were finally established outwards.

3.2. Occurrences of dissolved trace metals in the pearl river estuary and beyond

3.2.1. Upper rivers

Concentrations of dissolved trace metals were variable in the upper rivers (Mn: <6.8 nmol/L; Cu: 15–61 nmol/L; Cd: 0.11–0.99 nmol/L) (Table 1), reflecting the different extent of human perturbations. In particular, elevated dissolved metal levels (Mn: 6.8 nmol/L; Cu: 61 nmol/L; and Cd: 0.99 nmol/L) were observed in the North River (at the Shijiao hydrostation) reflecting an anthropogenic source from mining activities, e.g., the Dabaoshan copper mine nearby, the largest copper mine in Guangdong province (Fang et al., 2003). All the other river stations were characterized by lower concentrations of dissolved metals (Cd: 0.11–0.3 nmol/L; Cu: 15–20 nmol/L; Mn: <1 nmol/L). These values are lower than those in heavily perturbed urban rivers, e.g., the Ebro River in Spain (Schuhmacher et al., 1995), the Vistula River in Poland (Guéguen and Dominik, 2003), and the River Thames in England (Neal et al., 2006), but comparable with the values measured in the Amazon

(Boyle et al., 1982), and the Mississippi (Cd: 0.12–0.16 nmol/L; Cu: 23–24 nmol/L, Shiller, 1993). In summary, our results suggested that large rivers such as the Pearl River have overall experienced slight modifications in terms of dissolved metals due to increased human perturbations, whilst the impacts could be worse locally.

3.2.2. Groundwaters and coastline waters

The oxygen-depleted groundwaters showed decreased dissolved Cu and Cd levels (Cu: 7–17 nmol/L; Cd: 0.11–0.21 nmol/L) relative to the upper rivers (Table 1), which could be attributable to particle adsorption and precipitation as metal sulfides in the groundwater aquifers. Concentrations of dissolved Mn tended to be variable in the groundwaters depending on redox conditions: low in the upland groundwaters ($\sim$5–7 nmol/L), but high in the oxygen depleted lowland groundwaters ($\sim$1400–1600 nmol/L) (Fig. 5). Higher dissolved Mn concentrations in low oxygen groundwaters were also reported near Shenzhen (Chen et al., 2007). Such an increasing dissolved Mn trend in the groundwaters from upland to lowland was consistent with progressive Mn reduction coupled with organic matter decomposition along the groundwater flowpath (e.g., Roy et al., 2010). On the other hand, dissolved metal levels (Cd and Cu) were again elevated in some coastline water samples (salinity: 11.3; Cd: 0.6 nmol/L and Cu: 20 nmol/L), coupled with decreased Mn ($\sim$2 nmol/L) (Fig. 5), suggesting that these water bodies might also be subjected to the impacts of SGDs. Sulfate reduction has been reported in surface sediments of the estuary (Jiang et al., 2009), and elevated sulfides were commonly observed in the groundwaters near the lower estuary (e.g., in the city of Shenzhen, Chen et al., 2007). Once brought in contact with oxygen in water or air, those metal sulfides were oxidized, and therefore dissolved metals (e.g., Cd and Cu) were released from sulfides, leading to increased metal levels in the coastline waters.

3.2.3. Estuarine mixing zone

The upper estuary showed increased dissolved Cu levels (to as high as 40 nmol/L, Fig. 5), which could be attributable to sewage discharges from the nearby cities of Guangzhou and Dongguan, and stabilization of the Cu with fluvial organic ligands (e.g., Spiteri et al., 2008). Indeed, dissolved Cu has been used to reflect sewage discharges elsewhere, e.g., in the Peconic Bay (Breuer et al., 1999) and the Foundry Cove of the Hudson River (Mackie et al., 2007). Elevated dissolved Mn in the upper estuary (as high as 800–1660 nmol/L) further indicated a reducing environment, attributable to sewage discharges, in which reducing conditions were responsible for the dissolution of carrier phases like Mn oxides. Along with Mn reduction, metal ions such as Cu^{2+} were released into the water column. On the other hand, decreased dissolved Cd occurred in the upper estuary ($\sim$0.1 nmol/L, Fig. 5), probably due to the fact that H_2S was commonly high there ($\sum S = -10–150$ µg/L, Sheng et al., 2011) and CdS (Ksp=8.0×10^{-27}) was formed more easily than CuS (Ksp=4.0×10^{-21}) (Garrels and Christ, 1965). Alternatively, heavy metals like Cd can often occur as adsorbed phases on Fe-oxides/sulfides and can release to porewater during dissolution of minerals. Low levels of Mn but elevated Cd in the upper estuary may indicate that most of the reactive and thus bioavailable Mn-oxides get exhausted near shoreline (McManus et al., 2012) but Fe -oxides, the next one in the diagenetic sequence, enter into the upper estuary, dissolution of which may result in elevated Cd.

In contrast to the upper estuary, the oxygenated middle estuary was generally characterized by low levels of dissolved Mn (2–10 nmol/L) and high Cd (as high as 0.39 nmol/L, Fig. 5). The reductants (e.g. sulfides and reduced Mn^{2+}), transported from the
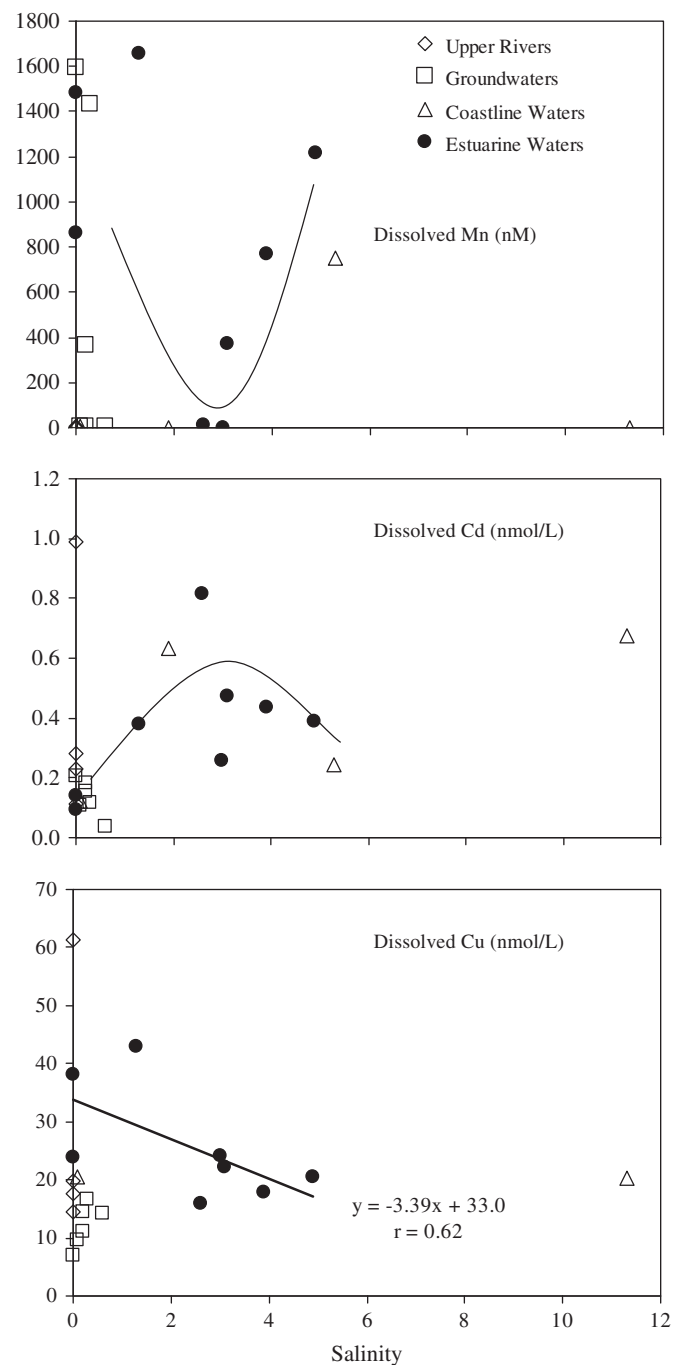
Fig. 5. Dynamics of dissolved Mn, Cd, and Cu vs salinity in the whole Pearl River Estuary system. The solid line shows the linear fitting of dissolved Cu against salinity in the estuarine waters.

upper estuary, were exposed to oxygen or nitrate in the water column. Progressively, Mn^{2+} ions were oxidized and precipitated as MnO_2, and dissolved Mn therefore decreased to <5 nmol/L (Fig. 5). However, no net removal of the metal ions (e.g., Cu and Cd) was observed along with the formation of Mn oxides during our survey, suggesting that other dominant source(s) exceeded the removal locally. Instead, dissolved Cu levels could still be as high as 40 nmol/L, and dissolved Cd (to as high as 0.8 nmol/L) was observed, which could be attributable to local anthropogenic sources or chloride-induced desorption from the resuspended sediments (e.g., Kraepiel et al., 1997; Robert et al., 2004) and the partial oxidation of metal sulfides. Such a dynamic pattern of dissolved metals was also commonly found in estuaries elsewhere,

e.g., in the Mississippi, USA (Shiller, 1993); and in the Seine estuary, France (Chiffoleau et al., 1994).

Dissolved Cu levels may be as low as $\sim$20 nmol/L, and dissolved Cd levels, $\sim$0.4 nmol/L in the lower estuary, indicating of estuarine mixing of PR freshwater and intruded SCS seawater. Indeed, dissolved Cu levels followed a negatively linear relationship with salinity in the lower estuary (dissolved Cu $= -3.39*$Sal$+33.0$, $r=0.62$, Fig. 5). Consistent with our inorganic carbon results, our study clearly demonstrated an absence of either important net excess or depletion during the estuarine mixing process in the lower estuary. In particular, the salinity values at the boundary of the estuarine and shelf waters only reached as low as $\sim$5. As far as the authors know, such a low salinity has never been reported previously (far less than previously reported values, e.g., salinity: $\sim$25 in the summer of 2000, Cai et al., 2004). The low salinity can reasonably be attributed to the high river discharge (which may reach as high as 37,000 m^3/s in the West River, 18.5 times as high as in the dry season) during our sampling period.

3.2.4. Shelf waters

Relative to the estuary, the shelf waters in the northern SCS contained much lower dissolved trace metal concentrations (range: Cd: 0.06–0.15 nmol/L, Cu: 0.3–1.0 nmol/L, and Mn: 3.0–13.0 nmol/L, Fig. 6). Sharp gradients from nearshore to offshore were shown for all dissolved metals: high nearshore (Cd: 0.15 nmol/L; Cu: $\sim$1.0 nmol/L; Mn: 13.0 nmol/L), but low offshore (Cd: 0.07 nmol/L; Cu: 0.4 nmol/L; Mn: $\sim$4 nmol/L) (Fig. 6). Enhanced concentrations of dissolved Cd and Cu nearshore indicated that the impacts of anthropogenic signals in the PRE had extended this far. High levels of Mn^{2+} nearshore may mainly result from Mn oxide reduction and porewater seepages (e.g., Roy et al., 2011) and a small proportion of anthropogenic sources if existed. Sharp gradients in Mn distribution

from nearshore to offshore may be simply due to the fact that most of the reactive and thus bioavailable Mn-oxides get exhausted during their transport from rivers to coast (McManus et al., 2012).

In contrast, the dissolved metal concentrations offshore (e.g., at the station A2: Cd: $\sim$0.07 pmol/L; Cu: $\sim$0.5 nmol/L, Fig. 5) were relatively low, and comparable to those in the open ocean, e.g., in the Pacific surface waters (Cd: undetectable-0.10 pmol/L; Cu: 0.4–0.54 nmol/L, Bruland, 1980); and in the central SCS (Cd: 50 pmol/L, Chen et al., 2005; and Cu: $\sim$0.6 nmol/L, Wen et al., 2006).

Dissolved metals (Cu, Mn, and Cd) play a critical role in phytoplankton growth (e.g., Morel et al., 1991). The high levels of Cu observed are likely to be more toxic than a micronutrient, while introduced Fe, Mn, and P may greatly relieve the nutrient stress of phytoplankton outside the estuary. Algal blooms periodically occurred in summer outside the lower estuary (e.g., Yin et al., 2000), and were generally characterized by chlorophyll-a values of 1–4 μg/L (e.g., Cai et al., 2002; Gan et al., 2009). During our survey, an extremely strong algal bloom (as indicated by high chlorophyll-a value $>$10 μg/L at the station 9: 114°E, 22°N, Fig. 6) was observed outside the estuary. Diatoms generally dominated (accounting for $>$90%), followed by Prasinophytes and Cyanobacteria here outside the estuary (detailed data not shown). Such a chlorophyll-a peak (2–3 times higher than in normal years) has never been reported outside the estuary previously. The salinity of 31 there observed from this study was also lower than values reported previously (e.g., $\sim$33.0, Gan et al., 2009). As well as station 9, the chlorophyll-a value was also high at station 8 ($\sim$1.4 μg/L; 114.2°E, 21.8°N) although the along-shore current had diluted the signals already. Phosphate typically ranged from 0.3–1.9 μmol/L in the estuary, while phosphate was undetectable ($<$ the detection limit of 0.08 μmol/L) outside the estuary (data are not shown), indicating that the phytoplankton growth in these waters were likely P-limited, as suggested by
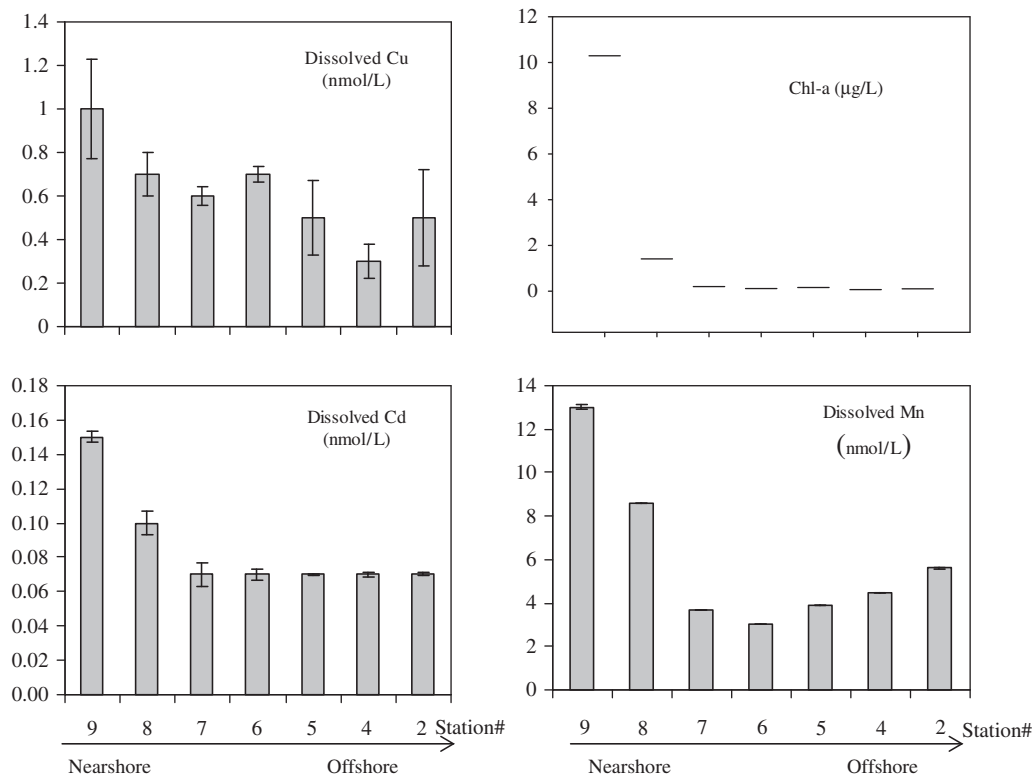

Fig. 6. Concentrations of dissolved metals (Cu, Cd, and Mn) and chlorophyll-a in the adjacent shelf waters of the northern South China Sea during the August 2009 sampling period (error bar: SD, $n=2$).

several previous reports (e.g., Yin et al., 2000; Ning et al., 2004). As a result, introduced P with high flow conditions was most likely responsible for the coastal algal blooms, which may have been removed by biological action whilst metals are not. We argue here that such an unusually strong algal bloom was attributable to the extremely high river discharge during our survey, and introduced micronutrients such as P (and Fe) (as indicated by enhanced dissolved metal levels) along with the estuarine flow could be responsible for coastal algal blooms.

3.3. Anthropogenic impacts in coastal waters

The PRE has been partly impacted by anthropogenic activities (e.g., Brigden et al., 2009). However, the upper estuary receives all the discharges from the East River, while the middle estuary receives the majority of freshwater from the West and North Rivers. Such freshwater inputs are critical since they can significantly decrease the dissolved metal levels simply by dilution. Along with large "pristine" freshwater inputs and sediment loadings, a series of geochemical reactions, including particle adsorption and transfer into the sediments, removed the majority of dissolved metals out of the water column in the estuary. Although sedimentary releases also occurred, a net sedimentary metal enrichment has been commonly observed in the PRE (e.g., Cheung et al., 2003).

As a result, dissolved metal levels were generally low in the PRE during our high river discharge sampling period, although these data are likely to represent lower limit values, and for much of the remaining part of the year, concentrations may be higher. In general, dissolved Cu and Cd in the PRE was even lower than in highly perturbed "small" coastal waters, e.g., the East River-Long Island Sound (e.g., Buck et al., 2005), the San Diego Bay, and San Francisco Bay (Flegal and Sañudo-Wilhelmy, 1993), and the Po-Adriatic Sea system (Danovaro, 2003). Dissolved metal levels were also less than the commonly recommended standards, e.g., Cu: 0.005 mg/L (75 nmol/L); Cd: 0.001 mg/L (25 nmol/L) from the People's Republic of China national sea water quality standard (Grade I, GB3097–1997). However, the enhanced dissolved metal levels observed in parts of the estuary clearly suggested that the PRE was in some places perturbed by the sewage and industrial effluent discharges, desorption of the resuspended sediments and the groundwater seepages. These contributions were relatively small in terms of the whole estuary, but not negligible locally.

Human perturbations are occurring widely in the world, e.g., extended hypoxia in coastal oceans (e.g., Diaz and Rosenberg, 2008), and elevated levels of dissolved metals (Cu, Mn and Cd) in the whole estuary observed in this study suggest that human perturbations have already impacted these aquatic environments from the upper rivers to the groundwaters until the coastline and estuarine waters.

The large contrast in river discharges between wet and dry years (which may have a difference of 18.5 times) in the Pearl River is a critical factor in transporting terrestrial materials into the ocean. The Pearl River Estuary is basically underlain by metal enriched muddy sediments, whilst these sediments are subject to repeated cycles of erosion under the channel incision and tidal intrusions (e.g., Lu et al., 2007). Anthropogenic signals, mostly associated with sediments, remain mainly within the PRE during dry seasons, but the high river discharge and especially an extreme event may transport these anthropogenic signals out of the estuary. When the summer southwest monsoon dominates, these signals (including metals and associated nutrients) can reach far into the adjacent shelf waters.

In addition, climate induced changes such as sea level rises, and changing precipitation patterns globally may also affect the extent and intensity of anthropogenic signals in coastal waters. For example, the sea level along the coast of the northern SCS has

risen at a rate of 2–3 mm/year during the past several decades (Tang et al., 2009). Such a sea level rise may then alter the water table and the groundwater circulation, potentially leading to remobilization of dissolved metals. In addition, Dore (2005) predicted that the global precipitation pattern could be further altered with extreme climates, i.e., the wet areas will become wetter while the dry and arid areas become more so. Such climate changes in the near future will potentially impact the groundwater seepages, and sediment mobilization, and even expand anthropogenic signals into coastal waters on a much larger scale.

4. Summary and conclusions

Dissolved trace metals (Cd, Cu, and Mn), along with oxygen and inorganic carbon, were for the first time systematically examined in the whole PRE from the upper rivers, the groundwaters to the coastline and estuarine waters. Although dissolved metal levels in the whole estuary were generally low due to large loadings of freshwater input, our results demonstrated that these water bodies in terms of dissolved trace metals have been perturbed to a small extent overall by human activities, but impacts could be serious locally.

The upper rivers were generally characterized by low concentrations of dissolved metals, in spite that high levels of dissolved metals (e.g., Cu: 61 nmol/L; Cd: 0.99 nmol/L) were observed in the North River due to mining activities locally. The groundwaters generally showed high dissolved Mn (as high as ~1600 nmol/L) especially in the lowland of the Pearl River Delta.

The whole estuary receives substantial amount of freshwater from the upper rivers, and these low-metal-content freshwater greatly diluted the anthropogenic signals, e.g., dissolved Cu and Cd (Cu: 14–43 nmol/L; Cd: 0.09–0.81 nmol/L), which was even less than those commonly polluted small estuaries. High levels of metals occurred in the upper estuary (e.g., Cu: 24–38 nmol/L) as directly receiving sewage and industrial effluent discharges from the mega-city of Guangzhou and nearby townships. Increased metal levels were also observed in parts of the groundwaters and the estuary, as these places were subject to dissolved metal mobilization such as oxidation of metal sulfides and the partial dissolution of minerals.

Under dry seasons, anthropogenic signals in the PRE mainly remained within the estuary, typically bound within the sediments. However, high river discharges (and, in particular, the extreme event with 18.5 times river discharge as much as in the dry season during our survey) can transport these anthropogenic signals out of the estuary, as indicated by elevated concentrations of dissolved metals outside the estuary in the northern SCS shelf waters (e.g., 114°E, 22°N: ~0.8 nmol/L of Cu; ~0.150 nmol/L of Cd; 13 nmol/L of Mn). Such levels of Cu might still not likely to be toxic to phytoplankton, whereas introduced nutrients including P (and Fe) under high flow conditions were likely responsible for the extremely high algal bloom observed there (chlorophyll-$a > 10$ µg/L).

In conclusion, our study demonstrated clear evidence for anthropogenic perturbations in terms of elevated dissolved metals throughout the Pearl River Estuary from the upper rivers, the groundwaters, until the coastline and estuarine waters, and even the adjacent shelf waters. In particular, high river discharges play a critical role in transporting anthropogenic signals out of the estuary on a large scale. During our sampling periods, dissolved metals (Cu and Cd) may not be limiting micronutrients triggering algal blooms outside the estuary, but nonetheless these metal signals can be used as indicators of the extent and intensity of human perturbation in such coastal waters.

Acknowledgments

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