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RESEARCH ARTICLE

Dynamics and geochemical responses of dissolved metals (Mn and Cu) in a subtropical estuary, China

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Abstract
The research delved into the occurrence and dynamics of dissolved metals, specifically manganese (Mn) and copper (Cu), within the Jiulong River Estuary, South China, a medium-sized subtropical estuary. Our findings unveiled a nuanced seasonal and spatial variability of dissolved metals throughout the entire estuarine system. Notably, dissolved Mn concentrations peaked (~3.5 μM) in the upper estuary, diminishing sharply along the salinity gradient, with a modest rise in the middle estuary and outer Xiamen Bay. In the upper estuary, heightened concentrations of dissolved Mn occurred in spring due to augmented terrestrial particle inputs, followed by suboxically reductive releases; conversely, concentrations were low in summer, attributed to dilution from increased freshwater discharges and particle scavenging. In contrast, dissolved Cu exhibited differently, with elevated concentrations (29.2–37.5 nM) in the upper and middle estuaries, driven by reductive dissolution of Mn particles and chloride-induced ion exchanges, respectively. Concurrently, heightened inputs of nutrients and metals correlated with elevated phytoplankton productivity (indicated by chlorophyll a) in the upper and outer estuary regions. Our analysis underscored the sensitivity of dissolved metals to environmental parameters, including temperature, pH, and dissolved oxygen. The integration of compiled historical data underscored the dynamic nature of dissolved metals, particularly Cu, in response to geochemical processes.The elevated ion levels indicated intensified ion releases from particles and sediments, attributable to increased anthropogenic perturbation and climatic changes (e. g. ocean warming).

Keywords Dissolved trace metals · Reductive dissolution · Chloride-induced ion exchange · Temperature rising · Jiulong River Estuary

Introduction

Trace metals such as Fe, Mn, and Cu are essential in phytoplankton growth in the ocean (Gao et al. 2000; King et al. 2011; Twining and Baines 2013; Twining et al. 2010). Trace metals could form cofactors in metalloenzymes in phytoplankton (Morel et al. 1991; Wang et al. 2012), functioning in carbon fixation (Fe, Mn), nitrogen fixation (Fe), and even intermetallic compensation (Sunda 2013; Twining and Baines 2013). Therefore, the deficiency of the metals could directly limit the algal growth (e.g., Fe), while the excess may also be harmful (e.g., Cu) to organisms (Fang and Wang 2022). In estuaries, terrestrial inputs, mainly via river runoff, delivered a substantial amount of trace metals which were further subject to be remobilized and/or scavenged before being discharged into the outer ocean (Jing 1995; Wang et al. 2012). During river-seawater mixing, hydro-chemical parameters including temperature, salinity, pH, and dissolved oxygen (DO) fluctuated and their dynamics directly influenced a series of geochemical processes (Wang et al. 2011a, 2012), including organic/inorganic complexation (Batchelli et al. 2010; Bruland and Lohan 2006), particle adsorption/desorption (Powell et al. 1996; Roy et al. 2011), and precipitation/remobilization (Fang and Wang 2022; Pokrovsky et al. 2014).

The Jiulong River is the 13th largest in China with an annual average discharge of 14.8 km^3 (Liang et al. 2019; Wu et al. 2019b). It provides water resources for nearby agricultural and industrial uses and drinking water

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for more than 3 million people in the highly populated southeast Fujian province, China (Yu et al. 2019a). The Jiulong River Estuary (JRE) is a semi-enclosed bay with semidiurnal tides and is characterized with wet (in summer) and dry (in winter) seasons due to the subtropical Asian monsoon (winter and spring) (Liang et al. 2019; Pan et al. 2021). The estuary received both metals and macronutrients from the upper river, with dynamic concentrations due to agricultural, industrial, and municipal activities, and even occasional eutrophication and algal blooms (Wang et al. 2012; Wang and Wang 2017; Weng and Wang 2014). Once being transported into the estuary, dissolved metals were further subjected to being adsorbed onto or forming organic, colloidal/suspended particles under dynamic hydro-geochemical conditions, and partially depositing into sediments (Fang and Wang 2022; Wang et al. 2011b). To some extent, the sedimentary metals were redistributed and transported/diffused upward in dissolved phases due to estuarine mixing and sediment disturbances (Jingchun et al. 2006, 2007; Tan et al. 2013; Tian et al. 2021; Wang et al. 2011b; Yan et al. 2022).

With rapidly increasing human activities in China over the past decades, the increased fluxes of pollutants including metals have directly or indirectly influenced the water quality and deteriorated aquatic environments. Anthropogenic metals could be traced as those from mining activities (Chen et al. 2018), the agricultural uses of commercial fertilizers and pesticides (Liang et al. 2019), aqua-cultural effluents (Tian et al. 2021), domestic sewage discharges (Wang et al. 2021), and industrial sewage sludge (Pan et al. 2022; Yu et al. 2019b) in the watershed. On the other hand, the water quality in the river and coastal environment has been greatly improved over the past years since China has conducted series of environmental protection policies.

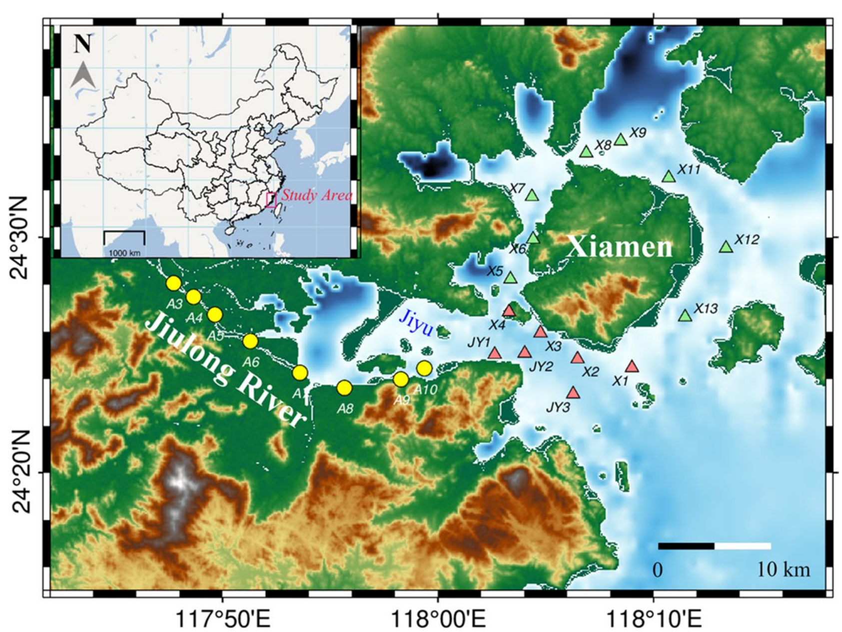
Estuaries are generally highly productive due to the large quantity of nutrient inputs from land runoff and coastal upwelling. In terms of subtropical medium-sized estuaries, the Jiulong river estuary is highly populated with nearby cities, receiving intensive effluences from anthropogenic activities from the river, sediment disturbances from navigation channels. Therefore, we conducted seasonal and spatial observations of dissolved metals along with hydrochemical parameters in the Jiulong River Estuary, aiming to fully elucidate the geochemical characteristics of dissolved metals in such estuaries, which might help us better understanding the role of such estuaries in the whole world ocean. We addressed the following issues in the estuary: 1) the occurrence and dynamics of metals in response to hydrological processes; 2) the geochemical processes controlling the metals' dynamics in the estuary; 3) historical trends of dissolved metals under climate change and anthropogenic pressure over the past decades.

Materials and methods

Study area

The study area includes the whole JRE and its offshore waters around the Xiamen Island (Fig. 1). The average monthly precipitation and water surface temperature in the study area were 4.07 mm day^{-1} and 25 ℃, respectively (Fig. 2a). Based on its geochemical setting, we divide the estuarine-coastal system into three sections (Fig. 1): ① the low salinity upper

Fig. 1 Map of sampling sites in the Jiulong River Estuary and the Xiamen Bay in China



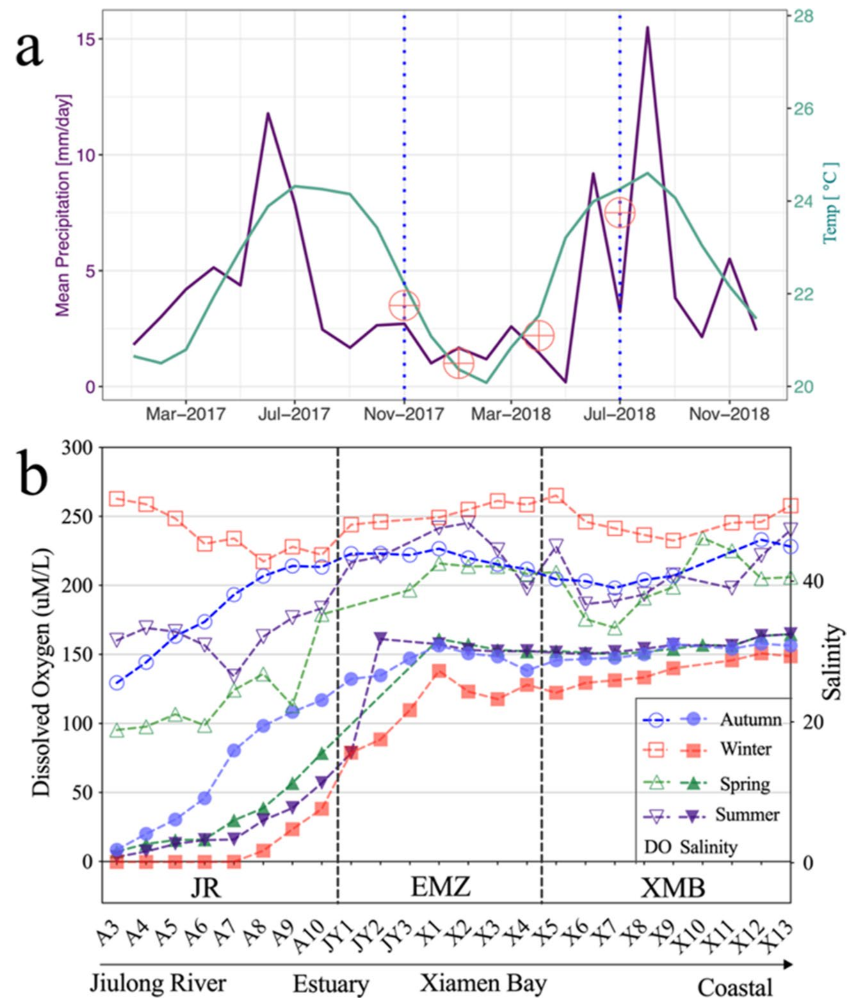


Fig. 2 The variation of hydrological and chemical parameters in the estuary. **a** Average monthly precipitation (mm day^{-1}) and surface temperature (℃) for the consecutive 2 years near (2017–2018) in the nearby hydrostations (data source: https://4dvd.sdsu.edu), red-cross dot represents the sampling date of four seasonal cruises. The four seasons observed are as the following order: autumn cruise (Nov. 2017, mean-flow season), winter cruise (Jan. 2018, dry season), spring cruise (Apr. 2018, mean-flow season), and summer cruise (Jul. 2018, flood season). **b** The salinity and dissolved oxygen (DO, μM L^{-1}) at surface waters from river to coastal seawater. The following three regions were defined based on salinity: JR, Jiulong River dominated low salinity zone (A3-A10); EMZ, estuarine mixing zone with high turbidity (JY1–JY3 and X1–X4); XMB, Xiamen Bay dominated coastal zone (X5–X13)

reaches of the JR estuary (JR, site A3–A10); ② the estuarine mixing zone with high turbidity (EMZ, site JY1–JY3 adjacent to Jiyu, and X1–X4); ③ the outer coastal waters including the Xiamen Bay (XMB, site X5–X13).

The monthly average precipitation (mm day^{-1}) and surface temperature (℃) for the consecutive 2 years (2017–2018) at the study area (24°30′ N, 118°50′ E; data source: https://4dvd.sdsu.edu) during the sampling period are presented in Fig. 2. During the sampling year, the annual mean temperature was 25 ℃, and the annual rainfall was 1484 mm, of which over 78.5% occurred in the wet season (June to November) (Fig. 2a). The regional climate is largely characterized with seasonal Asian monsoon and occasional typhoons in summer and autumn (Ren et al. 2001; Yu et al. 2019a).

Sample collection and processing

Four consecutive cruises in the same route were conducted in autumn (November 2017), winter (January 2018), spring (April 2018), and summer (July 2018) (Fig. 2) via the Research Vessel Haiyang II. A Go-Flo water collector (General Oceanics Co. Ltd, USA) was utilized to collect water samples at surface (~0.5 m below). The collected water samples (~150 mL) were immediately filtered (0.2 μm 47 mm PC, Millipore USA) into the acid pre-cleaned bottles on board. Trace metal clean techniques were employed to avoid contamination cautiously as much as possible (Wang et al. 2012).

Dissolved metals' analysis

The filtered samples were acidified to pH of < 2 with 6 M HNO_3 (Fluka Ultra) and stored for over 1 month. The acidified samples were then extracted and pre-concentrated by the Chelex 100 resin (100 mesh, Biorad, USA) and analyzed for metals using inductively coupled plasma–mass spectrometry (Agilent 7700, Agilent Technologies Inc., USA) (Wang et al. 2012). The certified reference materials (CRM) of river water (SLRS-6) and nearshore seawater (CASS-5) from the National Research Council of Canada were applied to assess the recoveries and validities of our analyses (Table S2), and all the recovery rates were within acceptable levels for all the metals (85% to 115%).

Table 1 Hydrological and chemical characteristics in surface waters during sampling seasons

Season	Zone	Depth (m)	Temp (℃)	Salinity	DO (μM)	pH	Chl-a (nM)	AOU
Autumn	JR	7.94 ± 1.45	23.2 ± 0.38	12.7 ± 8.34	181 ± 33.8	7.45 ± 0.27	5.35 ± 1.91	87.7 ± 51.8
	TSA	11.4 ± 3.25	22.3 ± 0.37	28.4 ± 1.76	224 ± 5.33	7.92 ± 0.07	2.74 ± 0.57	7.52 ± 6.02
	XMB	11.5 ± 6.41	22.2 ± 0.63	30.0 ± 0.99	208 ± 25.4	7.88 ± 0.11	2.65 ± 0.87	22.5 ± 24.2
Winter	JR	7.90 ± 2.49	15.6 ± 0.14	1.84 ± 2.85	238 ± 16.6	7.22 ± 0.22	6.10 ± 1.52	74.3 ± 13.7
	TSA	10.7 ± 3.52	15.7 ± 0.22	22.1 ± 4.19	258 ± 8.83	7.98 ± 0.12	2.22 ± 0.52	17.2 ± 14.1
	XMB	11.2 ± 7.09	15.1 ± 0.29	27.2 ± 2.00	251 ± 10.1	8.06 ± 0.03	2.17 ± 1.14	19.6 ± 11.3
Spring	JR	6.54 ± 3.43	25.6 ± 0.53	5.82 ± 4.94	128 ± 37.6	7.28 ± 0.29	4.57 ± 2.29	119 ± 44.1
	TSA	11.4 ± 4.63	23.3 ± 0.50	30.8 ± 0.81	217 ± 3.46	7.93 ± 0.04	2.10 ± 0.25	4.87 ± 2.51
	XMB	11.4 ± 7.35	23.4 ± 0.34	30.7 ± 1.02	206 ± 21.6	7.90 ± 0.09	4.02 ± 2.63	16.7 ± 22.3
Summer	JR	6.79 ± 3.72	31.7 ± 1.07	5.09 ± 6.12	164 ± 15.3	7.19 ± 0.25	12.2 ± 3.98	58.3 ± 18.9
	TSA	10.7 ± 3.91	30.0 ± 0.41	28.3 ± 2.83	228 ± 17.8	7.89 ± 0.07	7.44 ± 1.50	-26.8 ± 17.9
	XMB	11.9 ± 6.41	29.8 ± 0.23	30.9 ± 1.24	212 ± 20.4	7.89 ± 0.07	7.72 ± 1.88	-12.8 ± 20.2

Hydrological parameter analysis

The hydrological parameters including salinity, temperature, pH, and DO (listed in Table 1) were directly measured by a water quality analyzer (WTW Multi 3430, Germany) on board. The chlorophyll-a (Chl-a) samples (about 150 mL) were filtered directly with GF/F filters (Whatman) using a low-pressure pump (less than 150 mm Hg). The sample filters were instantly frozen in liquid nitrogen and then stored in a – 80 °C refrigerator, and later analyzed for Chl-a by using the fluorescence method (Parsons 1984).

Statistical analysis

Data processing and statistical analysis were performed using the SPSS software 23.0 (SPSS Inc., Chicago, IL, USA) and the statistics package R (Version 4.0.2, https://www.r-project.org). Cluster analysis (CA) and principal component analysis (PCA) were applied for better understanding the possible provenances of metals. The Spearman analysis was utilized to show the relations and interactions among each parameters.

Results and discussion

Hydrological and biogeochemical characteristics

The plot of dissolved oxygen (DO) against salinity (0–33) showed that DO generally increased with increasing salinity in surface waters of the estuary (Fig. 2B). DO varied seasonally: winter > autumn > summer > spring. The averages of DO, pH, and Chl-a were summarized along with water temperature, salinity, and depth, in the three sections (JR, EMZ, and XMB) reflecting of the normal seasonal changes

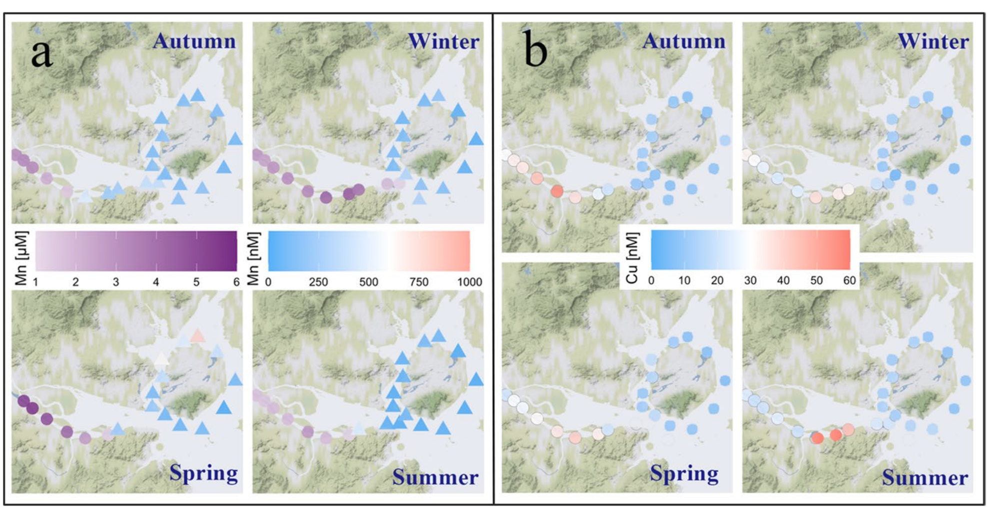


Fig. 3 The seasonal variations of dissolved Mn and Cu in μmol L^{-1} or nmol L^{-1} in surface waters of the estuary. The order for each season is listed below: autumn (Nov. 2017), winter (Jan. 2018), spring (Apr. 2018), and summer (Jul. 2018). **a** Dissolved Mn; **b** dissolved Cu

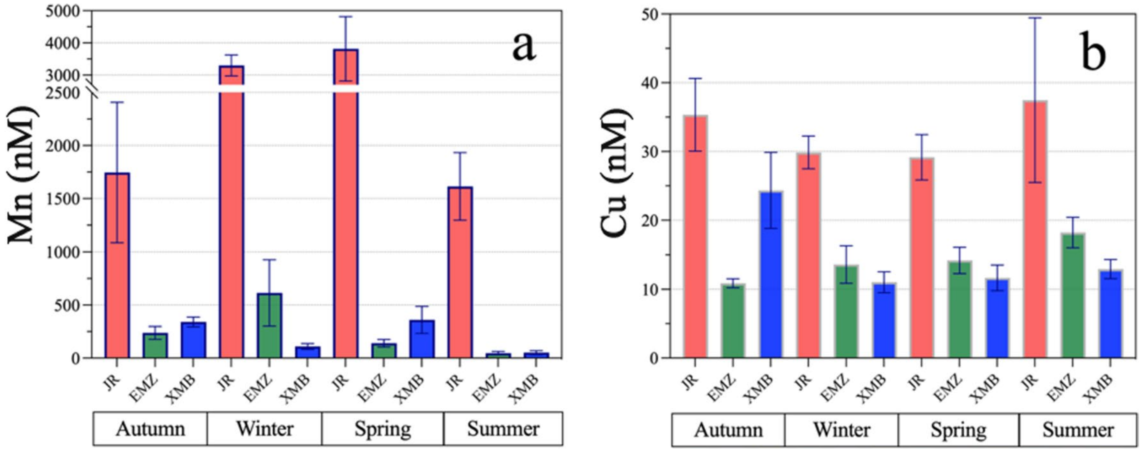


Fig. 4 The average concentration of dissolved metals in the different regions in the study. **a** Dissolved Mn; **b** dissolved Cu

(Table 1). Surface water temperature and Chl-a concentrations showed with a similar pattern: lower in winter (temp: ~ 15.5 °C; Chl-a: ~ 3.49 nM) and higher in summer (~ 30.5 °C; Chl-a: ~ 12.2 nM).

DO ranged from 128 to 258 µM and was low (87.5 µM) in the JR in spring, which was comparable with previous reports (78.1 µM) (Yu et al. 2019b). Estuarine waters were well oxygenated, as no hypoxia was observed (as defined as DO of < 62.5 µM) during all the sampling periods. The pH increased seaward from the river mouth to the estuary and then to the bay. The pH varied from 7.28 to 7.56 in the estuary and from 7.89 to 8.06 in the XMB. pH was strongly positively correlated with DO (R^2 = 0.77–0.98) in all seasons except in winter, suggesting both parameters are strongly coupled due to hydrodynamic fluctuations (Hu et al. 2022), but slightly affected with other activities including local acid deposition, wastewater discharge, and organic matter decomposition (Chen et al. 2018) in winter.

High algal abundance periodically occurred in summer as a result of increased riverine inputs of nutrients, as indicated by the increased Chl-a values of as high as 7.44–12.2 nM locally (Table 1). Previous researchers reported that diatoms and dinoflagellate commonly occurred during algal blooms in May, June, and July in the XMB (Chen et al. 2021). Algal bloom could also rarely occur in spring due to abnormal changes (February to April) (Weng and Wang 2014). Spatially, Chl-a varied in the three sections following the order: JR > EMZ > XMB in all seasons. Chl-a was generally 1–2 times higher in JR than in the two other zones, which was attributed to the fact that accelerated nutrient P inputs from upstream directly promoted the outbreaks of algae bloom (Xie et al. 2019; Yu et al. 2019b).

Dynamics of dissolved Mn and Cu

The averages of dissolved Mn (0.05–3.8 µM) and Cu (29.2–37.5 nM) were both higher in JR than the values

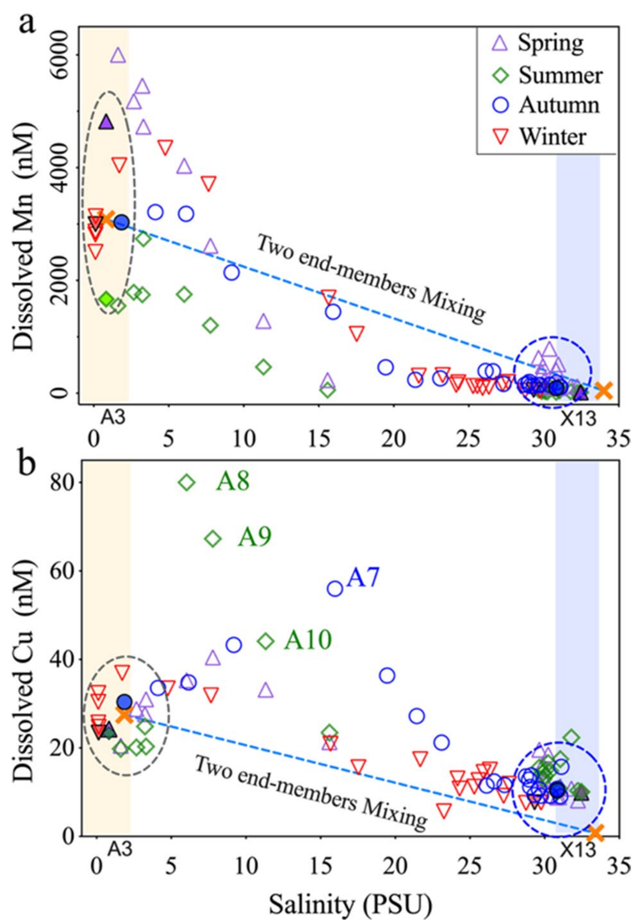


Fig. 5 The plot between dissolved metals and salinity for four seasonal cruises from river to coastal waters. The dashed line is the theoretical mixing line between river water (based on average values of the four seasons at A3) and seawater (based on average concentrations of the East China Sea for Mn = 5 nM and for Cu = 2.1 nM) (Seo et al. 2022). The two-end number sites (A3 and X13) are marked as solid symbols

Table 2 Comparison of riverine average concentrations of dissolved Mn and Cu in the Jiulong River estuary and largest estuaries worldwide

River and estuary	Length (km)	Discharge (km^3/year)	Mn (µM)	Cu (nM)	Reference
Jiulong River Annual	258	14.8	2.62	32.9	This study
Jiulong River in Spring	–	1.78	3.82	29.3	This study
Jiulong River in Summer	–	3.55	1.61	37.5	This study
Jiulong River in Autumn	–	7.39	1.75	35.3	This study
Jiulong River in Winter	–	2.08	3.30	29.8	This study
Nile River	6650	84	16.6	344	Badr et al. (2013); Wang and Polcher (2019)
Amazon River	6575	5800	0.2	35	Smoak et al. (2006)
Yangtze River	6300	1000	0.03	22.5	Wu et al. (2019a)
Mississippi River	6275	530	0.08	24	Shim et al. (2012)
Yenisei River	5539	673	0.14	–	Savenko and Pokrovsky (2019)
Yellow River	5464	56	1.82	62	Song et al. (2013)
Ob-Irtysh River	5410	427	11.7	30.3	Soromotin et al. (2022)
Parana River	4880	788	0.96	56	Pasquini and Depetris (2012)
Congo River	4700	1350	0.15	15.6	Martin and Meybeck (1979)
Amur River	4480	364	1.56	21.9	Chudaeva et al. (2011)

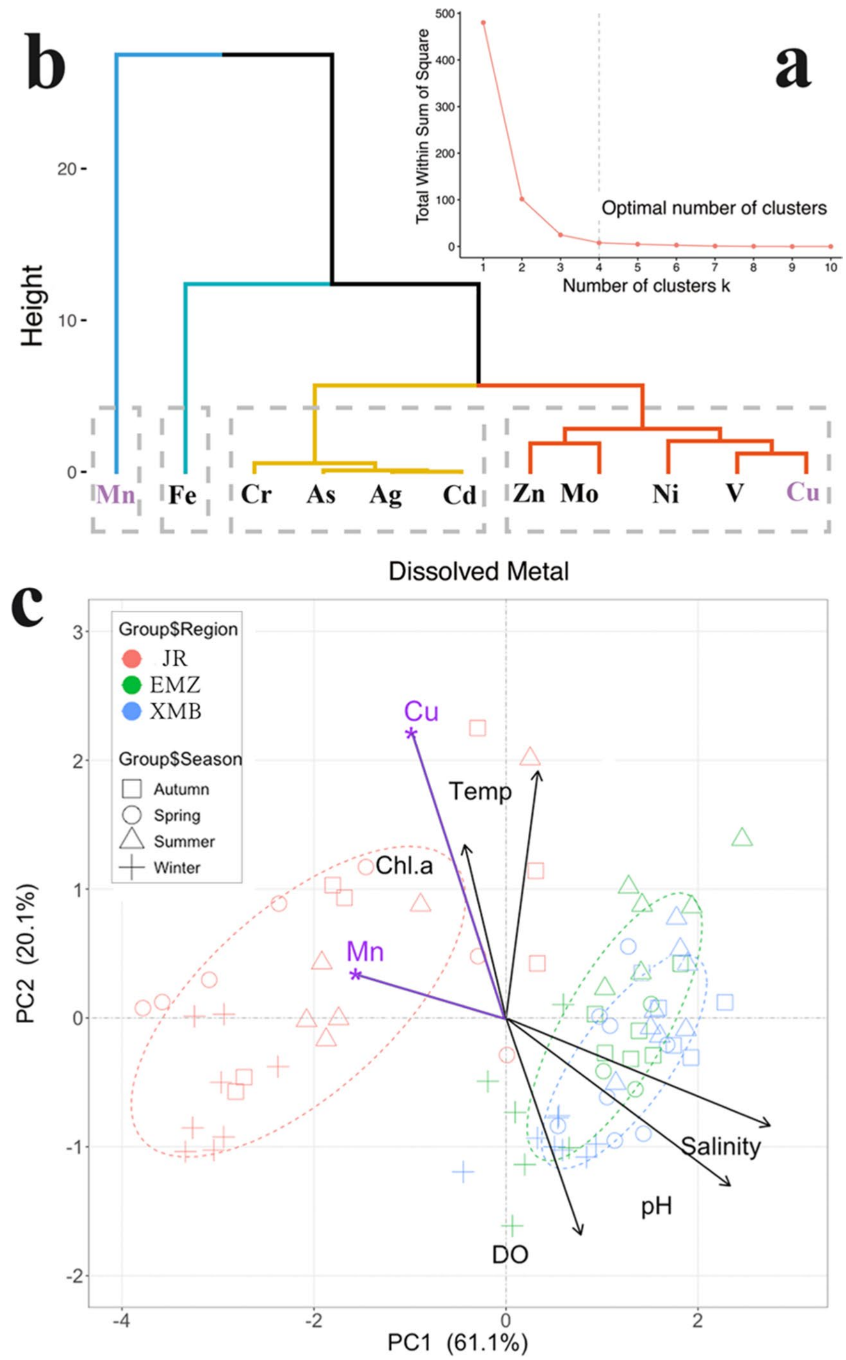
in EMZ and XMB for all seasons (Figs. 3 and 4). Cu concentrations reached a maximum at the mid-salinity zone (salinity of 4.77–21.4). Mn did not show any elevation in the mid-salinity or high-salinity zones. Instead, it decreased sharply with increasing salinity in all seasons (Fig. 5). Mn and Cu were partly depleted in the estuary (EMZ), which could be attributed to colloidal flocculation of organic matter (Batchelli et al. 2010; Bruland and Lohan 2006; Ruacho et al. 2022) and/or the utilization of phytoplankton (Jones 1974). Mn and Cu decreased from riverine to coastal waters, along with the salinity gradient (Fig. 3a and b), and the elevation of both metals' concentrations in the river end member could be attributed to anthropogenic and natural inputs from the river followed by sediment resuspension and reductive dissolution (Chen et al. 2018; Liang et al. 2019) during all sampling periods. Besides estuarine mixing, the lower concentrations of Mn and Cu seasonally also indicated the effect of dilution due to the freshwater inputs from JR (Wang and Wang 2016), and the scavenging onto or removal via particles.

The removal of dissolved Cu in the low-salinity zone could be partly related to colloidal coagulation and subsequent deposition into sediments (Fang and Wang 2022), but the distribution and seasonal variations of dissolved Mn might mainly be regulated by terrestrial inputs (Zhang et al. 2018). These metals like Mn and Cu, although with positive correlation between each other ($p < 0.01$, Fig. S2, except in summer), were subjected to different biogeochemical processes once arrived into the estuary (Weng and Wang 2014). Cu is heavily complexed by organic ligands in low saline zones while Mn is much more particle reactive in oxygenated waters, and redox sensitive, resulting in removal from solution via Mn oxyhydroxide formation accordingly (Harmesa et al. 2022; Ruacho et al. 2022). In particular, dissolved Cu was elevated in the middle estuary (10.9–18.2 nM), which was probably attributable to chloride-induced ion exchanges. These metals (Mn and Cu) behaved differently due to estuarine mixing, and responded differently to adsorption/complexation on Fe/Mn oxide particles and organic matter, and redistribution after suboxic or oxidation of these particles, which is consistently with previous reports elsewhere (Berrang and Grill 1974; Audry et al. 2006).

The concentrations of Cu and Mn in the JR, EMZ, and XMB varied in all four seasons (Fig. 4). Overall, Mn varied significantly in each season in the order of spring > winter > autumn > summer (Fig. 4a and b), indicating the higher inputs of oxide particles followed by reductive releases occurred in spring (Weng and Wang 2014). In contrast, rapid dilution and short flushing time in summer led to decreased concentrations of Mn and Cu (Millward 1995; Weng and Wang 2014). The higher Cu averages in summer than in autumn (opposite to Mn), reflecting that Cu might be subject to chloride-induced releasing from particles during maximum estuarine turbidity. Here we could not exclude the possibility that metals like Mn may partly come from human-induced releasing such as industrial effluent discharge locally (Liang et al. 2019; Zhang et al. 2018).

The concentrations of Mn and Cu in the JR in the summer were significantly ($p < 0.01$) higher than those in the XMB (Fig. 4), reflecting the elevated inputs along with the high river-runoff in the wet season. Besides, the seasonal dynamics of dissolved metals in the river endmember (Fig. 4b) may also

Fig. 6 Cluster analysis dendrogram and principal component analysis (PCA) for autumn, winter, spring, and summer cruises among dissolved trace metals and environmental factors in the surface waters of the whole Jiulong River Estuary. Note: A refers to the optimum numbers of clusters; B is the cluster analysis; and C is the PCA associated with environmental factor effects. Red color, JR; green color, TSA; blue color, XMB



partly reflect terrestrial inputs due to municipal effluents and/or groundwater releases (Adelson et al. 2001).

We summarized the average concentrations of dissolved Mn and Cu in the JR estuary (this study) and major estuaries worldwide (Table 2). Comparison of dissolved trace metals in the study area with other estuaries (Table S1) showed that the average Mn concentrations were slightly higher in the JR lower estuary than in the other estuaries in South China, such as the Pearl River Estuary. Cu showed with similar values as in other estuaries. The estuary provides the passage for delivering metals and acts as a geochemical reactor at the intersection of land and sea (Harmesa et al. 2022; Hu et al. 2022). Although the riverine runoff of the Jiulong River is within a medium size among world rivers, the concentrations of Mn were relatively higher in the JR estuary compared with other world estuaries, reflecting of the importance of increased anthropogenic disturbances from the nearby highly populated areas.

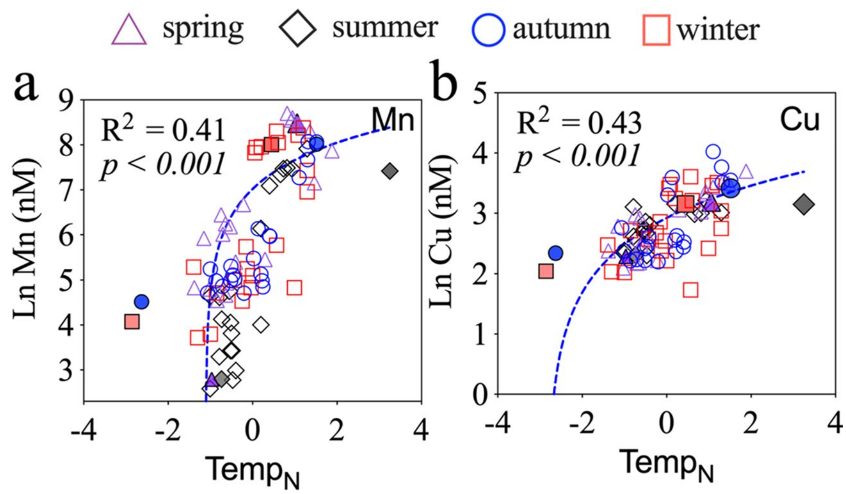


Fig. 7 The correlation of dissolved trace metals and temperature in the riverine-estuarine-coastal waters of four seasons in this study. All temperature data (where $Temp_N > 0$ indicates values above the average) were transformed to reach normalization by using the *Z*-score method, and the form of natural logarithmic variation (Ln) was applied to trace metals' concentration. The two-end number values are marked as solid symbols

Provenance analysis of dissolved metals

Other dissolved metals (except Mn and Cu) are presented against salinity in the supporting information (Fig. S1). Overall, Mn (1.61–3.82 μM) and Fe (32–327 nM) were higher in the whole estuary; Ni (8.51–91 nM), Mo (5.66–61 nM), V (9.56–28.9 nM), and Cu (29.2–37.5 nM) were lower; and Cr (1.52–15 nM), As (0.12–1.2 nM), Ag (0–0.15 nM) and Cd (0–0.6 nM) exhibited in the lowest values. Ni, Cd, and Cu all have a mid-salinity maximum, possibly due to Cl-ion complexation and ion exchange. Cluster analysis (CA) and principal component analysis (PCA) were performed to identify the possible sources of trace metals and their associated geochemical processes in the JR estuary (Fig. 6). The CA was employed in segmenting 11 dissolved metals in surface waters. As a result, the elements were grouped into four clusters (Fig. 6a and b): cluster 1 (Mn), cluster 2 (Fe), cluster 3 (Cr, As, Ag, and Cd), and cluster 4 (Zn, Mo, Ni, V, and Cu). A shorter distance in the clustered dendrogram indicates a closer relationship among trace metals. Accordingly, Mn was listed separately and not coupled with Fe, which could be explained as its association with major particle carrier (Mn oxides), contributing from natural weathering processes (Liang et al. 2019). In addition, dissolved Fe also behaved differently from the other elements which could be also attributed to its roles as major carrier for the transport of other trace metals (Mosley and Liss 2019).

PCA showed that the first two PCs explained 81.2% of the total variability of the examined trace metals and environmental factors (Fig. 6c). The analysis revealed all sampling sites could be classified into two categories: 1) the estuary and nearshore area (EMZ and XMB), and 2) JR (near the river endmember). The former showed an overlapping along the positive axis of PC1 (61.1%) in all seasons. DO, pH, and salinity have strong loadings on the positive axis of PC1 and were positively correlated to the EMZ and XMB samples. Cu and Mn were moderately negatively loaded with PC1. The latter showed with positive correlation between Mn and Cu (near the river endmember). Such coupling suggested that Mn and Cu likely have similar sources including the river discharge from particle dissolution and partly municipal/agricultural effluents. PC2 showed with high positive loadings of Cu but a weak loading of Mn, suggesting the metal (Cu) has specific characteristics in the estuary. Here we could not ignore the anthropogenic influences on each metal, and instead we suggest that each metal might experience different geochemical processes based on its chemical properties: e.g., high Cu could be mainly attributed to the chloride-induced desorption especially in the mid-salinity zone. In addition, the positive correlation of Mn and Cu with planktonic signals of Chl-a (Figs. S2 and 6) especially in the upper estuary suggested that, along with nutrients, these metals also facilitated the algal growth as essential elements.

Effects of hydrodynamic and biogeochemical processes

In estuaries, dissolved metals were commonly subjected to a series of geochemical reactions and also hydrodynamic disturbances. Both metals showed a significant difference between in the JR and EMZ/XMB, which indicated the complexity of hydrodynamic influences and geochemical effects during the mixing of freshwater and seawater. For example, high Mn occurred at the estuary in spring and winter, which could be attributed to the fact of decreased riverflow discharge and increased sediment resuspension during reductive dissolution. In contrast, high discharge in summer brought a large amount of suspended particulate which also scavenged metal ions besides the dilution effect (Zhang et al. 2008), leading to decreased Mn in summer.

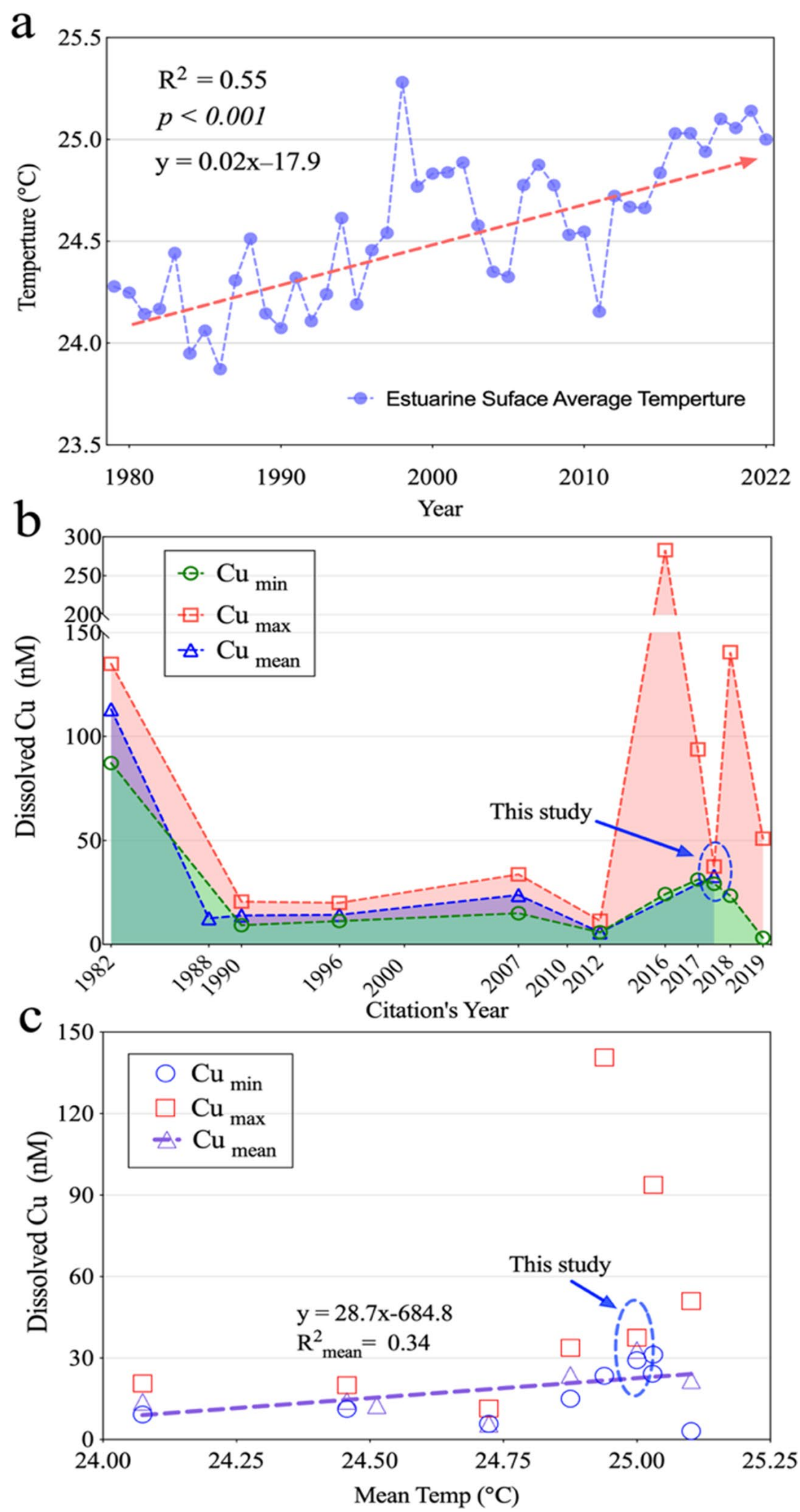


Fig. 8 Climate change evidence in global warming associated with dissolved Cu. **A** Jiulong River estuarine surface annual mean temperature during the years of 1980 to 2022; **B** dissolved Cu data in surface waters of the Jiulong River Estuary from previous researchers; **C** the correlation between the mean dissolved Cu and corresponding annual mean temperature. Data source: the historical annual temperature was collected from the database (https://4dvd.sdsu.edu). Previous dissolved Cu data were from the following researchers: Chen and Wu (1982), Huasheng and Jie (1990), Li et al. (1988), Gao (1996), Weng and Wang (2014), Wang and Wang (2016), Wang et al. (2017), Wang and Wang (2017), and Liang et al. (2019)

Chl-a is an important indicator of phytoplankton biomass and abundance in the ocean. During all seasons, Chl-a was high in the JR, and positively correlated with Mn and Cu in the JR in autumn and winter (Fig. S2). It suggested that estuarine mixing between two end members in the JR played a dominant role in the Chl-a distribution in autumn and winter.

Similarly, Mn and Cu showed a significant negative correlation with DO and salinity (Fig. S2) in the JR.

Negative correlations of metals with DO and pH suggested a series of proton-related processes dictating the dynamics of dissolved metals in the upper reach of the estuary: more cupric ions could be released under the condition of low pH and DO. Thereafter estuarine mixing became dominant in the estuary. Temperature negatively correlated with DO (Fig. S2), but positively correlated with Mn ($R^2 = 0.41$) and Cu ($R^2 = 0.43$, Fig. 7), which could be simply attributed to estuarine mixing. Along with compiled historic data, we observed that the water temperature in the estuary has increased almost 1℃ over the past four decades (Fig. 8a). After compiling with historic records of dissolved Cu, we observed that the trend of dissolved Cu also reflected the effect of temperature rising, climate change, and global warming. Notably, dissolved Cu concentrations in the JR estuary have increased in general based on the data from previous publications and positively correlated with the temperature over the past decades (Fig. 8b and c). Thus, we concluded that climate-change-related factors such as ocean warming could conceivably enhance the release of dissolved metals such as Cu in estuaries and coastal waters, or even in a larger extent.

Conclusion

This study investigated the seasonal variations in dissolved Cu and Mn concentrations and their geochemical characteristics in the Jiulong River estuary and Xiamen Island near shores. The middle estuary showed high concentrations of dissolved Cu, which could be attributable to ion exchange followed by particle desorption. Dissolved Mn showed the highest values (Mn: 3.8 μM) near the river mouth, followed by a sharp decrease outward, and a slight elevation in the middle estuary and outer Xiamen Bay. The study also found that Mn concentrations were variable in season as in the order spring > winter > autumn > summer. The highest Mn values occurring in spring might be simply attributable to increased inputs of high Mn-content particles from land runoff, followed by elevated reductive dissolution in spring. The lowest values in summer might mainly result from the diluted effect of higher freshwater discharge and increased scavenging onto particles and/or forming oxihydroxides. The study suggested that, in addition to natural weathering releases in the watershed, Mn and Cu also experienced a series of geochemical processes including ion exchange, organic complexation, and particle desorption/adsorption. Here anthropogenic activities including mining and industrial/municipal effluent discharges could also contributed to the elevation of these metal ions locally. Compiled with historical data, we observed that the concentrations of dissolved metals (e.g., Cu) have slightly increased over the past four decades, highlighting the possibility of dissolved metals being used as an indicator of climatic changes and increased anthropogenic perturbation.

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Author contribution Kang Mei: data curation, formal analysis, methodology, software, and writing—original draft; Mengqiu Shi: investigation and analysis; Nengwang Chen: resources; Deli Wang: writing—review and editing, funding acquisition, project administration, resources, supervision, and validation.

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Data availability Field data and R codes are available without registration form GitHub repository at https://github.com/meikangusa/Estuarine_Dissolved_Metal. Historical temperature and precipitation data are available at https://4dvd.sdsu.edu.

Declarations

Ethical approval No application for ethical approval is needed in this study.

Consent to participate Informed consent was obtained from all individual participants included in the study.

Consent for publication All authors approve the manuscript for submission and publication.

Competing interests The authors declare no competing interests.

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