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RESEARCH ARTICLE

Speciation of dissolved copper in human impacted freshwater and saltwater lakes

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Abstract China's natural waters are experiencing an increasingly anthropogenic perturbation widely including acidification and hypoxia, and toxic metals including copper (Cu) are subject to a series of reactions including chemical speciation and transformation. However, there is still little information available regarding such alterations of metal behaviors in China's natural waters. By using solid phase extraction technique, this study for the first time measured total dissolved Cu, and different Cu species: toxic labile Cu (referred to those free cupric ions and some weakly organic compounds adsorbed onto Chelex-100 resins), the organic refractory Cu (referred to those adsorbed onto C18 resins after passing through Chelex-100 resins), and residual Cu (obtained by subtracting labile and organic refractory fractions from the total) in a freshwater lake (the Lover) and a saltwater lagoon (the Yundang) in Xiamen, China. Our results demonstrated that both waters were characterized with relatively low levels of total dissolved Cu (5–10 nM), as a result of a net removal process dominated by particle adsorption and precipitation. Relatively high proportion of organic refractory Cu (as high as 50 %) was observed in the saltwater Yundang lagoon as a result of organic matter production and/or discharges followed by complexation nearby. On the other hand, the toxic labile Cu accounted for >40 % of the total dissolved Cu pool in these waters, and particularly the increased proportion of toxic labile Cu (as high as 70 %) occurred in the bottom sulfidic Lover Lake. Our study provides clear evidence that toxic labile Cu could be transformed under reducing environments such as deep sulfidic waters of the Lover Lake (Xiamen, China), and the releases of toxic labile metals are increasingly threatening nearby aquatic ecosystems.

Keywords Chelex and C18 resin solid phase extraction · Toxic labile and organic refractory copper · Anthropogenic perturbation · Chemical speciation · China's natural waters

Introduction

Copper (Cu) is commonly used as a pure metal or alloy in industrial activities and daily life around the world, and Cu compounds are also widely applied in agriculture or aquaculture as nutritional supplements or fungicides. Therefore, land runoff or direct sewage and industrial effluents could easily carry a large amount of Cu into nearby waters. Over the past decades, metal contaminants including Cu have been increasingly released into natural waters around the world, e.g., in the Long Island Sound (Beck and Sañudo-Wilhelmy 2007), and in the Pearl River estuary (Wang et al., 2012), in the South San Francisco Bay (Buck and Bruland 2005), in the Seine Estuary (Chiffoleau et al. 1994), and in the Scheldt Estuary (Paucot and Wollast 1997). Although a small amount of Cu is essential in algal metabolisms including photosynthesis (Morel and Price 2003; Peers and Price 2006) and high affinity iron uptake (Maldonado et al. 2006; Kustka et al. 2007), dissolved Cu beyond the tolerance levels could exert toxic effects to algal growth as in photosynthetic reaction and cellular division (Cid et al. 1995). In particular, those free cupric ions of as low as 10^{-11} mol/L might be toxic to certain phytoplankton species, such as cyanobacteria (Kozelka and Bruland 1998; Muller, 1996; Bruland et al. 1991).

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In natural waters, dissolved metals are subject to a series of geochemical reactions, including organic complexation, particle adsorption, and precipitation (e.g., Tubbing et al. 1994), which further alter the metals' availability and toxicity to aquatic systems (Kozelka and Bruland 1998; Brooks et al. 2008). On the other hand, these geochemical reactions are also subject to human perturbation such as subtle the temperature rise, and redox decreases in coastal waters, leading to more releases of toxic labile Cu from sediment porewaters into coastal waters (Beck and Sañudo-Wilhelmy 2007). Over the past decades, China has experienced a rapid economic development (Wang et al. 2014). Particularly, anthropogenic metal contaminants are increasingly emitted into nearby soils, aerosols, and sediments (Cheng 2003; Pan and Wang 2012). Eventually, a large amount of these metals reached nearby waters via land runoff, direct sewage, and industrial effluents. For example, the total discharges of metals (Cu, Pb, Zn, Cd, Hg, and As) into China's coastal waters reached the level of as high as 27,000 tons in 2012, among which Cu was 3700 tons (from China Oceanic Information Network, http://www.coi.gov.cn/). However, previous studies have mostly focused on those highly human impacted metal-enriched sediments (e.g., Duan et al. 2014; Xu et al. 2014; Zhang et al. 2012; Feng et al. 2011). There are still limited data available regarding dissolved metals in China's waters so far, e.g., in the rivers of Hainan (Fu et al. 2013), in the East China Sea (Li et al. 2014), in the Pearl River estuary (Wang et al. 2012), and in the Changjiang river (Yang et al., 2014; Shulkin and Zhang 2014), and even little published data are available regarding the chemical speciation and transformation of these metals such as Cu. As far as the authors know, there are only few articles examining the dissolved metal speciation in China (e.g., South China Sea, Wen et al. 2006; Danshuei River, Jiann et al. 2005).

This study selected two typical China's urban waters: the Lover freshwater lake and the Yundang seawater lagoon in the Xiamen Island, South China, and examined the total dissolved Cu and different Cu species (toxic labile, organic refractory, and residual fractions) along with hydrological and chemical parameters. The objectives of the study were to determine the speciation and transformation of dissolved Cu in these typical human impacted waters, and to explore the geochemical responses of toxic metals to the recently increasing human perturbation in China.

Materials and methods

Study area

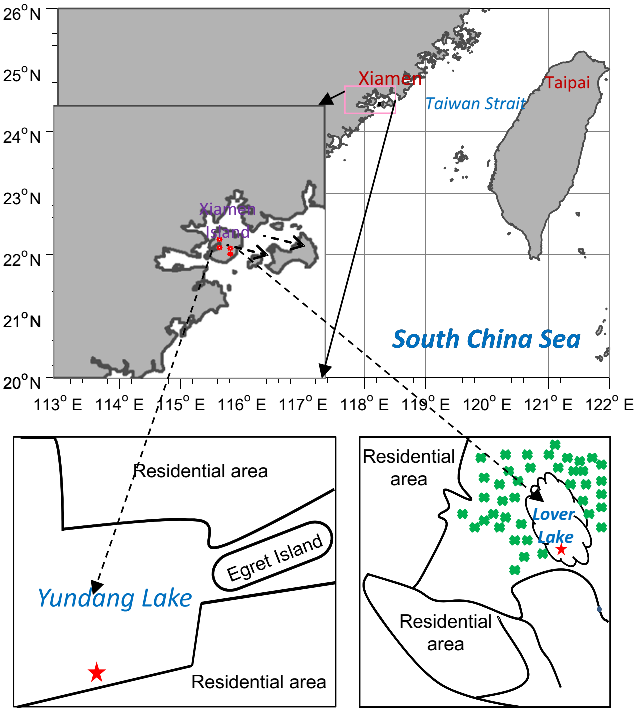

Fig. 1 Location of the Xiamen Island with the Yundang and Lover lakes indicated inside (*red star symbol* represent sampling sites)

The Lover Lake is located in a mountainous valley in the southern part of the Xiamen Island, with an area of ~38,000 m^2, and an average water depth of ~7.5 m and a 10-m deepest site (Fig. 1). The lake is surrounded with forests and receives freshwater from mountain streams, and influenced by human activities such as a floriculture greenhouse and a golf field nearby, and high land runoffs commonly occurred during heavy rain precipitation, characteristic of DOC concentrations of ~400 μmol/L. The surface water here appears brownish all the year around with high primary productivity (as indicated by high levels of Chl-a: 33–67 μg/L), and phytoplankton is dominated with the following species: *Scenedesmus quadricanda*, *Crucigenia quadrata*, *Oscillatoria tenuissima*, and *Melosira granulate* (Duan et al. 2011).

The Yundang Lake is located at the west side of the Xiamen Island (Fig. 1), with a surface area of 1.5 km^2, and an average depth of 2–3 m. The lake is actually a saltwater lagoon, connecting with seawater in the Xiamen Bay via a gateway. The Yundang Lake is subject to a substantial amount of municipal sewage discharges from the city of Xiamen. Particularly, the city of Xiamen has experienced a rapid industrialization and economic development for more than two decades with a population of ~3.67 million in 2012 (Xiamen Municipal Bureau of Statistics 2013). Chl-a was ~4.5 μg/L in the lake during our sampling period (Chen 2012), with the following algal species dominated: *Skeletonema costatum,* and *Euglena sp.* (Xu 2005).

Sampling

Field investigations were conducted in the lakes of the Lover and the Yundang on June 23, 2011 and March 22, 2011, respectively (Fig. 1). Water samples in the Lover Lake were taken from a water column of 10 m deep via using a peristaltic pump and plastic tubing marked at 1.0 m intervals. Similarly, the water samples in the Yundang Lake were obtained from a water column of 1.2 m deep at 0.2 m intervals. Filtered samples were collected first via capsule filters (0.22 μm). All the samples were collected in the order of increasing depth, and the water sample from the preceding depth interval was purged at each new depth by flushing the lines with ambient water.

Hydro-chemical parameters such as temperature, salinity, pH, and DO were determined on site by using a WTW analyzer. A portion of filtered samples were fixed in 0.5 M Zn-acetate on site and analyzed for H_2S in the laboratory using the methylene blue method (Cline 1969). Water samples for Chl-a 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 (Parsons et al. 1984).

Separation and measurements of different Cu species (toxic labile, organic refractory, and residual fractions)

Samples for dissolved Cu species were directly filtered on site into acid-washed PE bottles through acid-cleaned polypropylene capsule filter (0.22 μm). Once collected, the water samples were immediately returned to the laboratory. All the separation protocols were processed in a Class-1000 clean room laboratory at the State Key Laboratory of Marine and Environmental Science, Xiamen, China. The samples were processed within 6–8 h by using a two-column solid-phase extraction technique (resin Chelex-100 and C-18) under nitrogen condition adapted from Beck and Sañudo-Wilhelmy (2007).

Dissolved Cu in natural waters is generally composed of labile and refractory organically complexed and residual forms (e.g., Kozelka and Bruland 1998). The former (Chelex-adsorbed) refers to the "bioavailable" fraction including the free metal ions, inorganic complexes, and some small active organic molecules; the organic refractory (C18 adsorbed) mainly includes refractory organically bound complexes (Velasqueza et al. 2002; Waeles et al. 2004); and the last one refers to neutral organic molecules with little affinity with either Chelex-100 or C18 resins as defined as the residual fraction throughout the context. After extracted onto Chelex-100 and C-18 resins, Chelex-adsorbed metals (toxic labile) were eluted out with 10 mL 0.3 N HNO_3, directly into 30 mL wide-mouth LDPE bottles. C-18 columns were eluted with 10 mL methanol (Optima grade) into acid-washed 30 mL vials (organic refractory). All the eluates of Chelex-100 and C-18 columns were placed under a Class-100 clean hood and evaporated to dryness at the temperature of 60 °C. The dry sample residues (residual) were then reconstituted in 2 mL 0.3 N HNO_3 before analysis. All the samples were then analyzed on an Agillent ICPMS (State Key Laboratory of Marine Environmental Science, Xiamen University) by using standard addition techniques. The total dissolved Cu was obtained by summing all three fractions up. The detection limits for all the dissolved Cu species were estimated by three times of the standard deviation of triplicate procedural blanks with <0.1 nmol/L. The accuracy of the total dissolved metal determination was checked with the certified reference materials (river water SLRS-4 and coastal water CASS-4) with <5 % deviation.

Results and discussion

Hydro-chemical settings in the lakes

All the hydro-chemical parameters and the dissolved Cu speciation data in the two lakes are summarized in the Appendix Table 1. Our results showed that the freshwater Lover Lake was generally stratified throughout the water column, with a thermocline layer at 2.0–4.0 m during the sampling period (June 2011) (Fig. 2). The water temperature was 30 °C in the upper lake waters, and 23 °C in the deep lake waters. In addition, the upper water body was characterized with high oxygen and pH (<2.0 m $O_2 > 8.0$ mg/L, pH >8.2) as exposed to atmospheric oxygen and with a high primary productivity (indicated by relatively high Chl-a: 33–67 μg/L), while the deep water body was characterized with extremely low oxygen and pH (4.0–9.0 m <0.3 mg/L, pH = 6.1–6.9). Particularly, high levels of sulfides (42–65 μmol/L) occurred in the deep waters (4.0 m until bottom) (Fig. 2) suggesting of a sulfidic setting there.

In contrast, the saltwater Yundang Lake was fully aerobic with high oxygen levels (5.2–07.1 mg/L) throughout the water column during our sampling period (March 2011) (Fig. 2), probably as influenced from the strong seawater intrusion from the Xiamen Bay. In addition, the Yundang Lake was characterized with high salinity (24–26), relatively low levels of Chl-a (4.5 μg/L, Xu 2005), slightly high pH (7.3–7.6), low temperature (15–16 °C), and low levels of H_2S (undetectable to 0.4 μmol/L) throughout the whole water column.

Speciation of dissolved Cu

Our study showed that the concentrations of dissolved Cu were generally low in these urban lakes (4–10 nmol/L), and varied slightly in our study waters: 8.5 ± 2.2 nmol/L and 4.1 ± 0.5 nmol/L in the upper and deeper waters of the Lover Lake, respectively, and 9.1 ± 2.2 nmol/L in the Yundang Lake (Fig. 3). In general, dissolved Cu concentrations were lower than those in moderately human perturbed waters (Fig. 4), e.g., in the Mississippi delta (23 nmol/L, Shiller and Boyle 1991); in the Delaware River (37 nM, Church and Scudlark 1997); the Long Island Sound (10–40 nmol/L, Buck et al. 2005); the Danshuei River (25–60 nmol/L, Jiann

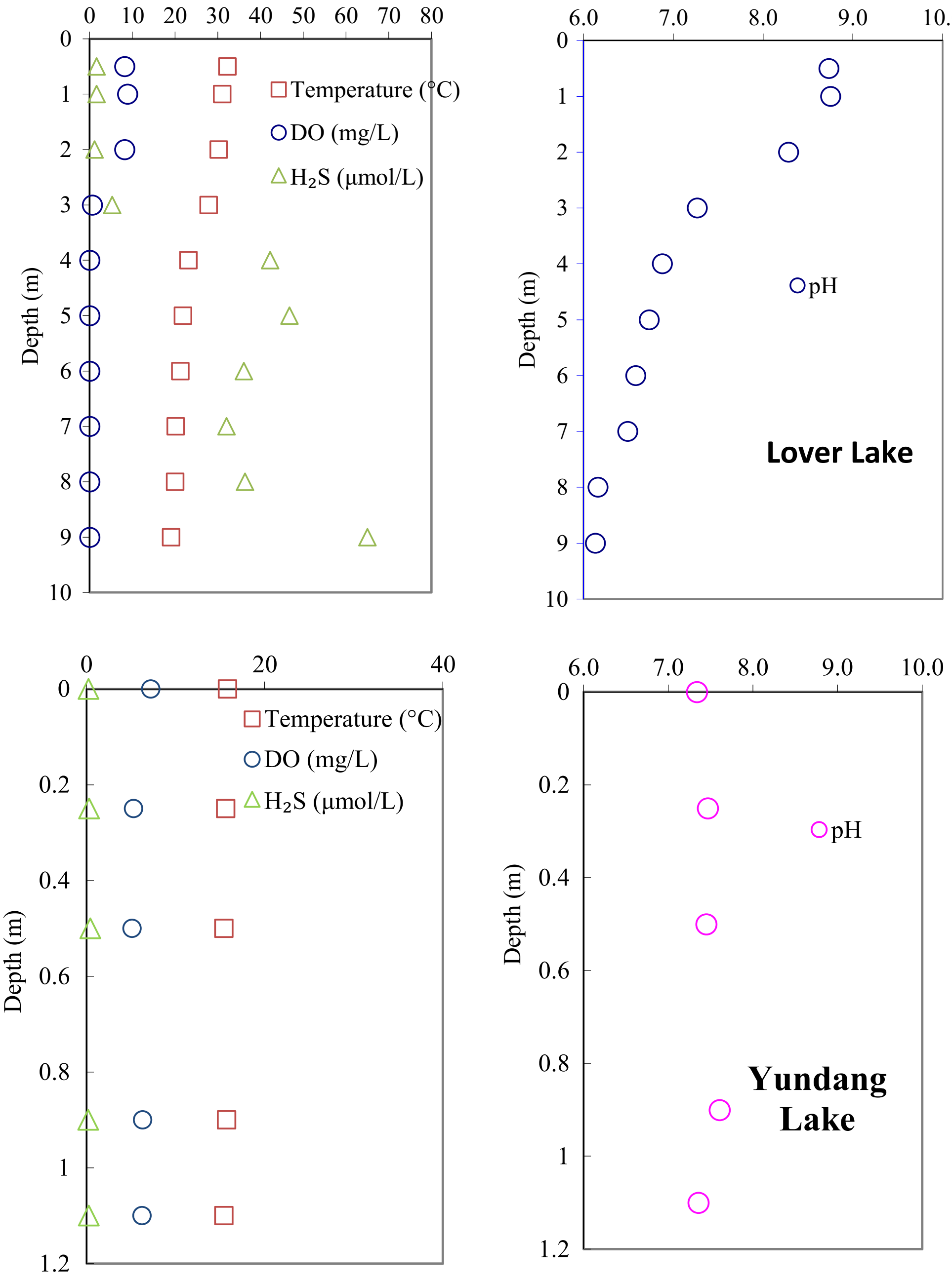

Fig. 2 Vertical profiles of temperature, pH, DO, and H_2S in the Lover and Yundang lakes. *Shaded rectangular areas* represent the transition zone in the Lover Lake

et al. 2005); the Seine Estuary (10–60 nmol/L, Chiffoleau et al. 1994); the Scheldt Estuary (5–60 nmol/L, Paucot and Wollast 1997), the South San Francisco Bay (47 nM, Buck and Bruland 2005), and the Great South Bay, NY (30 nM, Beck et al. 2010).

Relative low concentrations of dissolved Cu in both Lover and Yundang waters could not simply be attributed to low inputs of anthropogenic inputs, particularly due to the fact that sewage discharges from the city of Xiamen were severely loaded into the Yundang Lake and nearby waters (e.g., Chen 2012, 2009; Zhou et al. 2010), and the sediments in the lake and nearby waters were heavily enriched with heavy metals such as Cu (Lin et al. 2009). In addition, high levels of pollutants also commonly occurred in the Lover Lake as a result of land runoff during heavy rains (Zhou et al. 2007), and both lakes were characterized with high levels of suspended sediments and organic materials (Wang et al. 2006; Lin et al. 2011). Indeed, riverine fluxes of particles were high in nearby waters, e.g., the sediment fluxes from the Jiulong River contributed a substantial amount of materials to coastal waters including the Xiamen Bay (244 × 10^4 tons/year, Cai et al. 1999). The Yundang Lake was characterized with high levels of total suspended matter (a few to 50 mg/L, Lin et al. 2011), and total suspended matter could also be as high as 14–16 mg/L in the

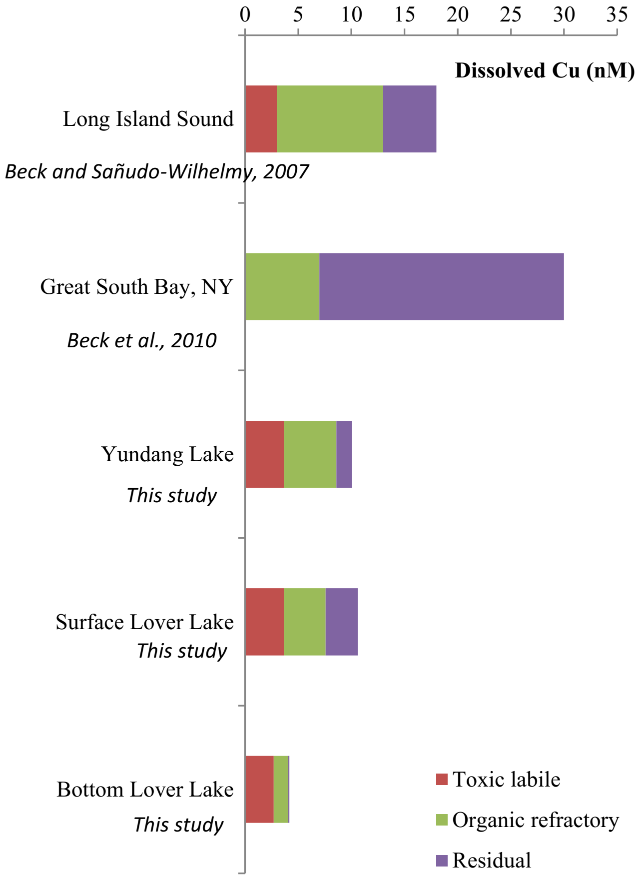

Fig. 3 Comparison of dissolved Cu compositions in the lakes of Lover and Yundang with those in coastal waters of USA and other waters in China

Lover Lake (as observed in our study). High discharges of organic materials due to terrigenous runoff, sewage, and anthropogenic effluents also occurred in the nearby waters (e.g., ~21,000 tons COD_{Mn}/year, Wang et al. 2006). Therefore, metal contaminants were subject to particle adsorption and/or organic complexation in these water bodies, as suggested elsewhere previously (e.g., Davis 1984). Consistently, the coupling of comparatively low dissolved Cu levels with high sulfide in the deep sulfidic Lover Lake waters (sulfide 42–65 μmol/L; Cu 4.1 ± 0.5 nmol/L) suggested that Cu was mainly removed and precipitated as sulfides (e.g., CuS or Cu_2S), and finally accumulated into sediments, as consistent with previous studies in the lake sediments (Lin et al. 2011).

Similar to the total dissolved Cu, different dissolved Cu species also behaved dynamically in these waters. Generally, organic refractory Cu ranged from 1.0 to 6.0 nmol/L, accounting for 30–50 % of the total dissolved Cu. Organic refractory Cu was also different in these waters: 2.9 ± 0.7 nmol/L, and 1.1 ± 0.2 nmol/L in the upper and deeper waters of the Lover Lake, and 4.1 ± 1.1 nmol/L in the Yundang Lake, respectively. These organic refractory Cu species was probably produced during organic discharges nearby, e.g., sewage effluents in the Yundang Lake, and land runoff in the Lover Lake, as consistent with previous reports in the Danshuei River estuary (e.g., Jiann et al. 2005). Residual Cu was mostly undetectable (<0.1 nmol/L) in the Lover Lake, and elevated concentrations of residual Cu occurred at the depth of 2.0 m (4.5 nmol/L) along with high TSM (12–16 mg/L). Residual Cu mainly occurred (as high as 2.1 nmol/L) near surface in the Yundang Lake and decreased downwards until undetectable. These residual Cu species might also be related to direct sewage discharges or land runoffs locally, and alternatively residual Cu could also be produced from organic materials via bacterial decomposition.

Toxic labile Cu was higher in the upper waters (4.0 ± 0.5 nmol/L) than in the deep waters of the Lover Lake (2.9 ± 0.6 nmol/L) and was 3.8 ± 1.2 nmol/L in the Yundang Lake (Fig. 4). As the dominant species in the Lover Lake, toxic labile Cu accounted for ~49 ± 13 and ~70 ± 7 % in the upper oxic and bottom sulfidic zones, respectively (Fig. 4) and ~40 % of total dissolved Cu in the Yundang Lake. Our results showed that the proportions of labile Cu were higher than those in the USA (<20 %), e.g., in the Great South Bay (Beck et al., 2010) and in the Long Island Sound (Beck and Sañudo-Wilhelmy 2007, Fig. 4).

Toxic labile Cu might contribute from direct sewage effluents, and upward diffusion from sediment porewaters. Alternatively, the higher proportion of toxic labile Cu in these China's natural waters could also be partly attributable to the production from organic refractory Cu. For example, toxic labile Cu in the bottom waters might result from the reduction of organic materials in those sulfidic environments, while the photoreduction of organic refractory to labile Cu also occurred in the top surface waters as consistent with previous reports, e.g., in the low-latitude waters (Voelker et al., 2000). In addition, toxic labile Cu in bottom waters could diffuse upward from sediment porewaters into the overlying waters (e.g., Beck and Sañudo-Wilhelmy 2007).

Transformation of organic refractory to labile Cu and its possible mechanism

Dissolved metals, however, generally exist in natural waters as in several chemical species including labile, organic refractory, and residual fractions. These different chemical species behaved quite differently in terms of their particle affinity and reactivity (e.g., Turner et al. 1998; Charriau et al. 2011). For example, Charriau et al. (2011) reported that organic complexation might stabilize the metals in dissolved phases, while free metal ions could be readily precipitated with sulfides. Turner et al. (1998) also suggested that dissolved metals have low particle affinity once complexed with non-labile organic materials.

In addition to the direct sewage source, dissolved Cu undergoes a series of reactions including chemical speciation and transformation. These reactions could be largely dictated by environmental factors like temperature, pH and Eh, and

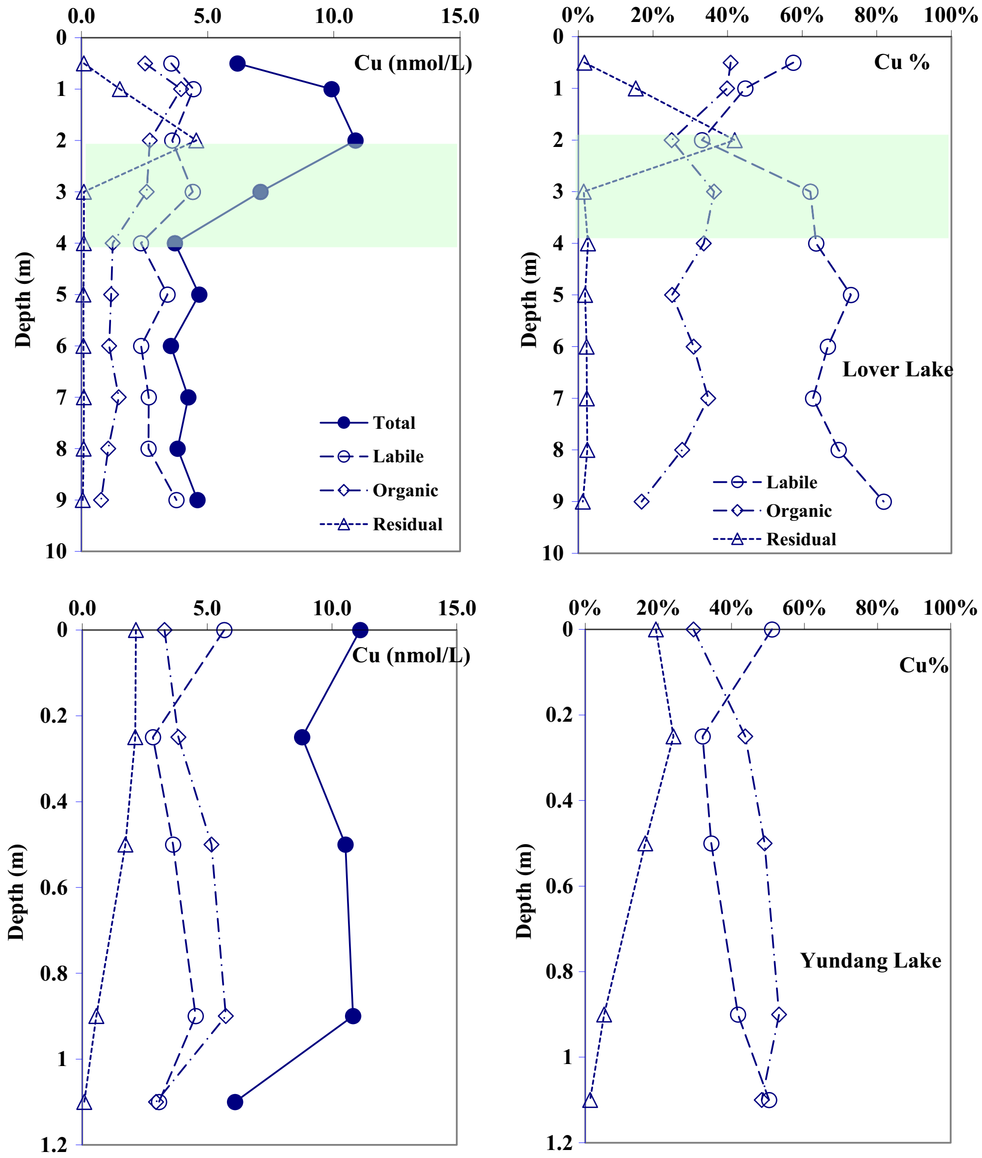

Fig. 4 Vertical variations of total dissolved Cu, labile, organic and residual fractions (*upper panels*), and percentages of each species in total (*lower panels*) with increasing depth in the lakes of Lover and Yundang. *Shaded rectangular areas* represent the transition zone in the Lover Lake

even biogeochemical processes such as autochthonous organic matter production and remineralization (e.g., Zuo et al. 2012; Zhao et al. 2014; Tonietto et al. 2015). For example, highly reducing conditions favored the production of labile metals (e.g., Beck and Sañudo-Wilhelmy 2007), and high temperature conditions also trigger upward releases of labile metals from porewaters (e.g., Beck and Sañudo-Wilhelmy 2007). The high proportion of labile Cu in our study waters along with in other China's natural waters (Fig. 3) suggested of its production from organic refractory Cu, leading to a net accumulation of labile Cu in these sulfidic waters. On the other hand, toxic labile Cu is also subject to precipitate out of water column under the conditions of high sulfides (e.g., Charriau et al. 2011), and via high affinity with particles (e.g., Turner et al. 1998). Under those strongly sulfidic conditions, the insoluble sulfide precipitates (e.g., CuS and Cu_2S) could be readily formed (Dyrssen and Kremling 1990; Brugmann et al. 1997), due to the extremely low solubility product of CuS 6×10^{-16}. Therefore, high levels of H_2S in the deep sulfidic Lover Lake waters ultimately led to a net removal of dissolved Cu as precipitating free cupric ions out of the water column (Fig. 2).

In natural waters, dissolved Cu could precipitate out of the water columns following two reactions: deassociation of organic refractory Cu (as represented as $Cu = C_{org}$) to toxic labile Cu (as represented as Cu^{2+}) under high levels of hydrogen ions, and then adsorption of toxic labile Cu onto particles, or precipitation as solid sulfides:

$$Cu = C_{org} + 2H^{+} \rightarrow Cu^{2+} 2H^{+} - C_{org}{}^{2-}$$
$$Cu^{2+} + CO_3{}^{2-} \rightarrow CuCO_3$$
$$Cu^{2+} + H_2S \rightarrow CuS + 2H^{+}$$

In particular, toxic labile Cu could be largely precipitated out of the water column under sulfidic conditions, while in those acidific waters, more proportion of labile Cu could also be dissoluted from organic refractory Cu via ion exchanges. As a result, more toxic labile Cu accumulated. China's natural waters experienced a series of humane perturbation over the past years including intensified hypoxia in coastal waters (e.g., Dai et al. 2006), acidification of freshwater in land (e.g., Zhang and Chen 2002), and even hypoxia in freshwater and coastal waters (e.g., Zhang et al. 1999). Our study provides clear evidence that such alteration in terms of hydrogen ions and redox conditions could potentially impact the water chemistry including the cycling of the metal Cu, and particularly lead to a net accumulation of toxic labile Cu, threatening aquatic ecosystems.

Conclusions

By using the solid phase extraction technique, we for the first time separated labile and organic Cu species from the total dissolved Cu pool in two typical lakes in China. The results show that total dissolved Cu was relatively lower in our study waters (4–11 nmol/L) than those moderately human impacted waters, as influenced from a higher land runoff with suspended particles and organic materials in these waters. In addition, our results also show that dissolved Cu is subject to precipitate out of the water column as sulfides in those strongly reducing waters such as the bottom sulfidic Lover Lake. Organic refractory Cu could directly originate from sewage discharges and land runoffs, and organic refractory Cu could also be formed after organic complexation of free cupric ions.

Particularly, we observed with elevated levels of toxic labile Cu in these natural waters. These toxic labile Cu could be produced from the di-association of organic refractory Cu under high levels of free hydrogen ions via ion exchanges. In addition, high proportion of toxic labile Cu could also be produced during the precipitation of Cu sulfides. Therefore, along with the further acidification and redox changes in China's natural waters, toxic labile fraction of dissolved Cu is expected to increase with the potential of impacting aquatic ecosystems in a larger extent in the near future.

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Appendix

Table 1 Hydrological data and dissolved Cu speciation in the lakes of Lover and Yundang

Lover Lake									
Depth (m)	Temp (°C)		pH	DO (mg/L)	H_2S (μmol/L)	Labile Cu (nmol/L)	Organic refractory Cu (nmol/L)	Residual Cu (nmol/L)	Total dissolved Cu (nmol/L)
0.5	32.2		8.7	8.2	1.6	3.6	2.5	0.1	6.2
1	31		8.8	8.8	1.6	4.4	4.0	1.5	9.9
2	30.2		8.3	8.1	1.1	3.6	2.7	4.5	10.9
3	27.8		7.3	0.6	5.2	4.4	2.6	0.1	7.1
4	23.1		6.9	0.0	42.2	2.4	1.2	0.1	3.7
5	21.8		6.7	0.0	46.7	3.4	1.2	0.1	4.7
6	21.2		6.6	0.0	36.1	2.4	1.1	0.1	3.5
7	20.1		6.5	0.0	32.0	2.7	1.5	0.1	4.2
8	20		6.2	0.0	36.4	2.7	1.1	0.1	3.8
9	19		6.1	0.0	65.0	3.8	0.8	0.1	4.6
Yundang Lake									
Depth (m)	Temp (°C)	Sal	pH	DO (mg/L)	H_2S (μmol/L)	Labile Cu (nmol/L)	Organic refractory Cu (nmol/L)	Residual Cu (nmol/L)	Total dissolved Cu (nmol/L)
0	15.8	24.1	7.34	7.2	0.2	5.7	3.3	2.1	11.1
0.25	15.6	25.9	7.47	5.3	0.3	2.8	3.9	2.1	8.8
0.5	15.4	26.7	7.45	5.1	0.4	3.6	5.2	1.7	10.5
0.9	15.7	26.7	7.61	6.3	0.2	4.5	5.8	0.6	10.8
1.1	15.4	26.7	7.36	6.2	0.3	3.1	3.0	0.1	6.1

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