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ORIGINAL PAPER

Occurrence of copper-complexing ligands in the coastal sediments of eastern Red Sea

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Abstract The speciation of copper in seawater is greatly influenced by the presence of organic ligands that find their way from various sources. The occurrence of copper-complexing ligands in the coastal sediment of eastern Red Sea and their potential resuspension under the impact of physical parameters such as wind and currents are investigated. The competitive ligand exchange and detection of copper by adsorptive cathodic stripping voltammetry (ACSV) were used to determine the dissolved concentration of copper-complexing ligands and their conditional stability constants after suspension of marine sediments in UV-irradiated seawater. The laboratory experiments of suspended marine sediments in UV-irradiated seawater followed by the measurements of copper in the filtrate have indicated the presence of two ligands with concentrations in the range of 3.53–25.58 nM g^{-1} for L_1 and 8.33–28.35 nM g^{-1} for L_2 whereas the log conditional stability constants ranged between 12.59 and 13.87 for log K_1 and 11.79 and 12.96 for log K_2. Comparison of log K_2 with values for log K of copper complexes with thiols from previous studies suggests that thiols consist of the major part of copper-complexing ligands in the coastal marine sediments of eastern Red Sea. Relatively, positive and good correlations are found for copper-complexing ligands with total copper and organic content in the sediments. Calculation of the flux of copper-complexing ligands and their contribution to the total budget in the coastal water south of Jeddah indicate that the impact of sediments as potential source is less than 13 %. It is therefore that other processes such as in situ production and input from sewage effluents have to be considered to account for the majority of dissolved copper-complexing ligands in the area.

Keywords Eastern Red Sea · Coastal sediments · Copper-complexing ligands

Introduction

Our understanding of trace metals biogeochemistry in the oceans increased in the mid-1970s due to the “new reliable data” that resulted from precautions in sampling and advanced analytical techniques (Chester 2003). The earlier data had focused on the total dissolved concentration of trace metals with a few studies oriented to study the chemical forms of trace metal “speciation.” Later on, studies on trace metal speciation attracted the attention of oceanographers, and it has been shown that the biogeochemical cycles of trace metals are related to their speciation rather than total concentration (e.g., Bown et al. 2012). Studies on copper speciation covered various marine environments from coastal (Laglera and van den Berg 2003; Buck and Bruland 2005; Muller and Batchelli 2013; Oldham et al. 2014) to oceanic waters (Coale and Bruland 1988, 1990; Donat and van den Berg 1992; Midorikawa and Tanoue 1998; Moffett and Dupont 2007). These investigations have shown that copper is highly bounded to organic ligands and organic complexation of copper consists up to 99 % of total dissolved copper in seawater. The high affinity of copper to organic ligands reduces the concentrations of free ionic copper to ultra low values (picomolar concentrations). Therefore, organic complexation is the main factor in controlling the levels of free ionic copper in seawater. Some other factors including the adsorption/complexation of copper on the surface of particulate organic

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matter and/or possibly on iron/manganese oxide particles are also believed to affect copper speciation (Kerner and Geisler 1995; Gerringa et al. 1998; Fernández Severini et al. 2009; Al-Farawati et al. 2011; Roussiez et al. 2011).

Most studies of the organic complexation of copper in seawaters have focused on the distributions and processes in the water column, where a significant fraction of copper-complexing ligands are likely to be produced through biological activities (Zhou and Wangersky 1989; Moffett and brand 1996; Croot et al. 2000). However, sediments could be a potential source of both trace metals and organic ligands (Skrabal et al. 1997, 2000; Chapman et al. 2009; Santos-Echeandía et al. 2013). In most studies on dissolved copper complexation with organic ligands, up to two classes of copper binding organic ligands have been detected. It was suggested that in situ production is the source of stronger copper organic ligands whereas riverine input and diffusion from shelf sediments are the major carrier of weaker copper organic ligands (Muller et al. 2001). Porewater measurements were used to evaluate the flux of copper-complexing ligands from Chesapeake Bay sediments, and the flux ranged between 0.3 and 1.2 μM m^{-2} day^{-1} whereas the flux of dissolved copper was less by 40-fold, indicating that most of the copper is complexed by organic ligands. The magnitude of the benthic fluxes of copper-complexing ligands in the Bay ranged between 10 and 50 % of the pool of copper-complexing ligands in Chesapeake Bay (Skrabal et al. 1997). Recently, the daily flux of copper-complexing ligands due to tidal currents was investigated in non-vegetated and vegetated area for Tagus Estuary, and it was found that the flux in vegetated area (48.2 μM m^{-2} day^{-1}) was higher by around 15 orders of magnitude than the non-vegetated area (Santos-Echeandía et al. 2013).

Our aim is to study the potential releases of copper-complexing ligands from coastal sediments of eastern Red Sea. Since bottom currents in the marine environment are known to re-suspend the marine sediments, our laboratory experiments are based on simple suspension of marine sediments in UV-irradiated seawater. The copper-complexing ligands and conditional stability constants were evaluated in filtrate using adsorptive cathodic stripping voltammetry (ACSV) (Campos and van den Berg 1994). The supporting parameters such as organic carbon content, total copper, carbonate content, and grain size category in sediments were also measured and are correlated with copper-complexing ligands in order to understand their role on the biogeochemical cycle of copper.

Materials and methods

Study area

The sediment samples (five samples) were collected along the eastern coast of Red Sea (Fig. 1). One sample was collected from Haqel in the north (St. HQ1). Four samples were collected along Jeddah coast: North Corniche (St. NC2), Reayat Al-Shabab Lagoon (St. RS3), Al-Arbaeen Lagoon (St. AR4), and South Corniche (St. SC5). This geographical variation represents different depositional environments of various characteristics. The stations HQ1, NC2, and SC5 are coastal stations which are more open to the sea; therefore, the physical parameters (e.g., winds and currents) are expected to have major impact on the sediment characteristics. The other two stations, RS3 and AR4, are coastal lagoons with restricted water circulations. Settings of these stations also vary due to the impact of human activities on their environment. The human impact on coastal environment of Haqel (St. HQ1) is less than that of Jeddah coast (Sts. NC2, RS3, AR4, and SC5). This is due to a population of 30,000 people in Haqel compared to a population of 3.4 million people in Jeddah (www.jeddah.gov.sa and http://www.cdsi.gov.sa/english/). The environmental parameters in coastal environments of Jeddah indicate that the area is polluted at various levels. The most pronounced feature is the high levels of contaminants that were recorded in the coastal lagoons of Reayat Al-Shabab Lagoon (St. RS3) and Al-Arbaeen Lagoon (St. AR4) and are attributed to the discharge of untreated sewage and restricted water circulation (Basaham 1998; El-Rayis 1998; El-Rayis and Moammar 1998; El Sayed 2002a; Turki et al. 2002). The South Corniche receives a daily amount of 300,000 m^3 of partially treated sewage from Al-Khumra Sewage Treatment Plant (El Sayed 2002b; Basaham et al. 2009; Al-Farawati 2010). However, the municipality of Jeddah has used a multiport diffuser pipe dispersing system which enhances the dispersion of the contaminants. The North Corniche suffers from discharges of untreated sewage from different sources due to recreational activities (e.g., hotels and chalets).

Sample collection and treatment

The surface sediment samples were collected from stations (Fig. 1) during April 2010 using grab sampler. The samples were placed in sealed polyethylene bags and transported to the laboratory in icebox. The samples were dried overnight at the room temperature on a clean bench and subsequently grounded using a gate pestle and mortar. Finally, subsamples were used for the analysis of various parameters.

Instrumentation and analytical procedures

The measurements of total dissolved copper and complexation parameters (copper-complexing ligands and the conditional stability constants of copper-organic complexes) were undertaken using a μAutolab voltammeter (ECO Chemie, The Netherlands) connected to a Metrohm VA 663 electrode (Metrohm, Switzerland) and controlled by a personal computer. The reference electrode (Metrohm, Switzerland) was a

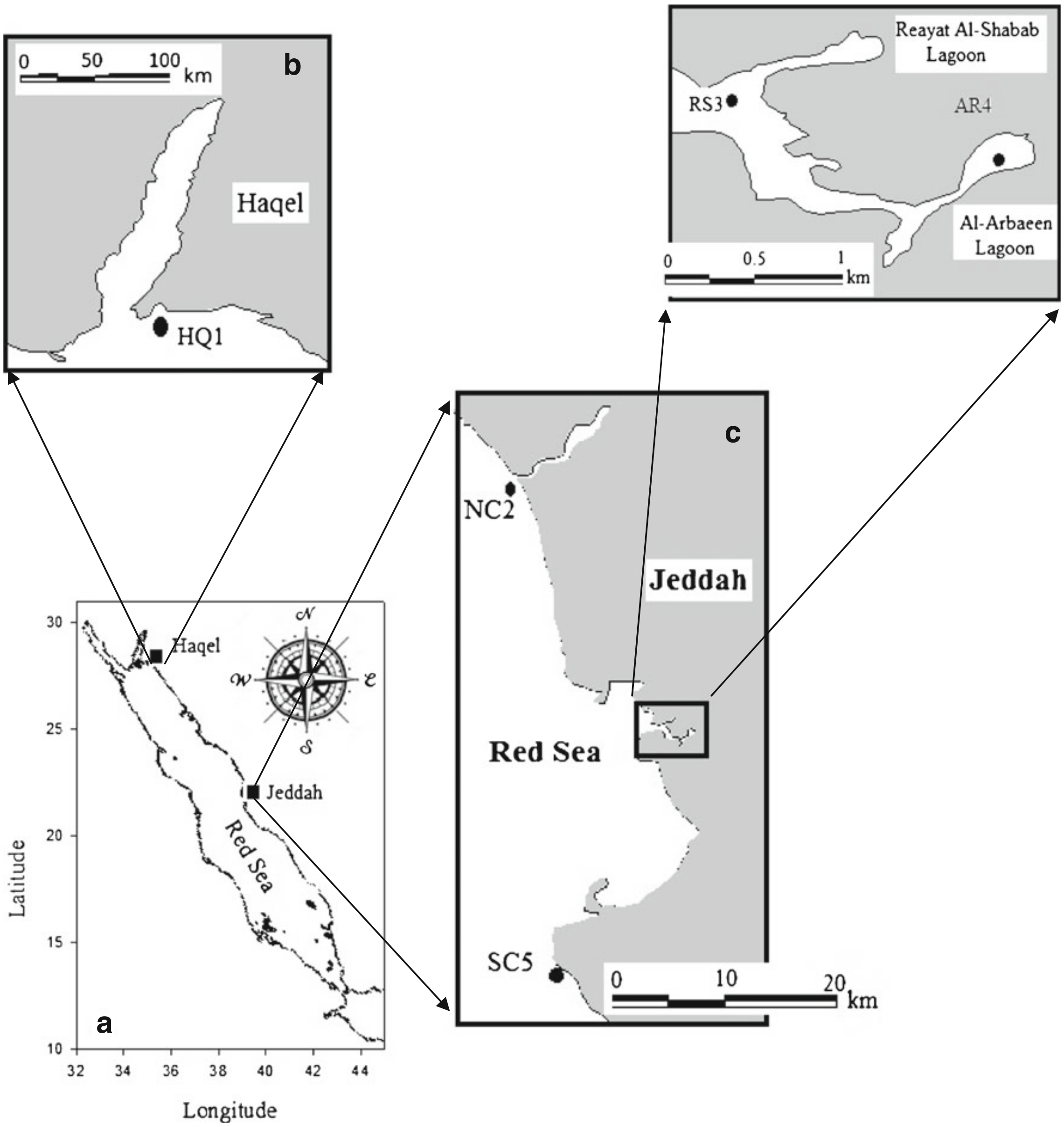

Fig. 1 The geographical locations of sediment samples during April 2010. **a** Location of Jeddah and Haqel along eastern Red Sea. **b** Location of sediment sample from the coast of Haqel. **c** Locations of sediment samples from the coast of Jeddah

double-junction Ag/AgCl (3 M), and the counter electrode (Metrohm, Switzerland) was a glassy carbon rod. The interference of dissolved oxygen in the samples was removed after treatment of the samples with a high-purity nitrogen gas for a period of 5 min. Destruction of organic compounds was achieved using 500-W high-pressure mercury vapor lamp constructed at oceanography laboratories in Liverpool, UK, coupled with 30-ml silica tubes (Achterberg and van den Berg 1994). The pH measurements were undertaken using a Metrohm 744 pH meter and calibrated against a pH 4 and 9 on the NBS pH scale. The voltammetric cell was rinsed at the beginning of the measurement with diluted acid followed by Milli-Q waters. The measurement of dissolved organic carbon (DOC) was undertaken using Shimadzu TOC-VCPH analyzer. Carbonate content in the sediments was estimated by treating a known weight of the air-dried sediment with 0.2 M HCl (1/25 *w*/*v*). Carbon dioxide evolved was measured using a calcimeter. Carbonate concentration in the sample was calculated using standard pure$CaCO_3$. Organic carbon content in sediments was measured using the sulfo-chromic wet oxidation method (Le Core 1983). Powdered sediment was first treated with phosphoric acid at 110 °C to get rid of carbonate and chloride ions; then, organic matter was oxidized with a mixture of potassium dichromate and sulfuric acid. The excess dichromate was then back titrated with sodium thiosulfate. The quantity of the thiosulfate corresponds to a definite quantity of total organic carbon, which is then attributed to the weight of the sediment sample. For the determination of total copper in sediments, powdered freeze-dried subsamples were digested using a nitric/hydrofluoric/perchloric acid mixture in the ratio 3:3:1 (*v*/*v*) (Basaham 1998). Digestion was carried out using a microwave digestion unit. The acid was evaporated to near dryness, and the residue was taken in 0.1 M HCl. Concentrations of total copper were determined using thermal atomization technique GFAA (PerkinElmer Analyst 800). Determination of grain size of the sediments was carried out using the standard dry sieving technique. Sediments were classified according to mud-sand-gravel ratio (Flok 1980).

Reagents

All reagent solutions were prepared in Milli-Q by weighing the appropriate salt into sterilized polystyrene tubes (30 ml) or Nalgene high-density polyethylene (HDPE) bottles. The final volume of the solutions was adjusted by weight. A stock solution of salicylaldoxime (SA) (0.01 M) was prepared in 0.1 M HCl. A stock solution of borate buffer solution (1.5 M) was prepared by dissolution of boric acid in NaOH solution (0.4 M) and was UV irradiated to eliminate organic compounds. Addition of 50 μl of buffer to 10 ml of seawater gave a pH of 8.2 (NBS pH scale). The decision of using borate buffer was taken after measurements of the pH of seawater from the study area (pH ~8.1). Copper standards were prepared by dilution of atomic absorption spectrometry standard solutions (BDH, Spectrosol grade) in Milli-Q water and acidified to pH ~2.5 by addition of HCl. Acids were purified by sub-boiling distillation in quartz still.

The impact of time on the releases of DOC

Various weights (0.5, 1, 2, and 5 g) of marine sediments were suspended in 130 ml of UV-irradiated seawater. The samples were placed on a shaker, and the concentration of DOC was measured at time intervals of 1, 2, 4, 8, 16, and 24 h.

Procedure to determine total dissolved copper using ACSV

ACSV was used for the determination of trace metals. In ACSV, the metals are chelated with a suitable complexing agent and then adsorbed or deposited on the hanging mercury drop electrode (HMDE) (van den Berg 1989). SA was used as complexing agent for determination of copper (Campos and van den Berg 1994). Acidified seawater was UV irradiated prior to the total dissolved copper determination. An aliquot of 10 ml seawater was pipetted into the voltammeric cell; 100 μl borate pH buffer (final concentration 0.01 M) and 25 μl SA (final concentration 25 μM SA) were added. The solution was deaerated by purging for 5 min with high-purity nitrogen gas. The deposition potential was set to −1.1 V; four mercury drops were discarded before a new mercury drop was extruded, and the solution was stirred for a preset period of 1 min. Then, the stirrer was stopped and a quiescent period of 10 s was allowed before switching the potential to −0.15 V to re-oxidize the deposited and plated copper. Then, the potential scan was initiated from −0.15 V and was terminated at −0.6 V. The peak height of copper was recorded and calibrated with standard copper. The accuracy of method was tested by analyzing nearshore seawater reference materials for trace metals (CASS-4). Our results were within 15 % of the certified values.

Copper-complexing ligand titrations

Acid-clean HDPE bottle (capacity of 250 ml) was used to suspend 2 g of a sediment sample in150 ml UV-irradiated seawater that has been collected from the coast of Jeddah. The concentration of total dissolved copper, initially present in the seawater, was determined (~2 nM copper) using ACSV. The sample was placed on a shaker for 24 h, and the seawater was filtered using acid-clean cellulose nitrate filter (0.45 μm). One hundred twenty milliliters of filtrate was transferred to acid-clean high-density polyethylene bottle (capacity of 250 ml), and borate buffer and SA were added at final concentration of 0.01 M and 5 μM, respectively. Copper was added to an acid-clean polystyrene bottles (30 ml) giving a concentration range between 0 and 800 nM (in 10 ml seawater) in ten steps; 10 ml aliquots of filtered seawater (of previous step) were then pipetted into the acid-clean polystyrene bottles (30 ml) and left overnight for equilibrium. The electrochemical signal of copper was measured using ACSV.

Evaluation of copper-complexing ligands

The concentrations of copper-complexing ligands and conditional stability constants of copper complexes with organic ligands were determined by titration of the samples with copper. ACSV takes the advantage of competition between the organic ligands released from the sediment and added complexing ligand (SA) to the added copper in the sample. Linearization of titration data is the key for the calculation of copper-complexing ligands and conditional stability constants of copper-organic complexes (van den Berg and Kramer 1979; Ruzic 1982; van den Berg 1982):

$$\frac{[\mathrm{Cu_{labile}}]}{[\mathrm{CuL}]} = \frac{[\mathrm{Cu_{labile}}]}{\mathrm{C_L}} + \frac{\alpha'}{K'_{\mathrm{CuL}}\mathrm{C_L}}$$

where [CuL] is the concentration of copper complexes with organic ligands L, $[\mathrm{Cu_{labile}}]$ is the labile copper concentration, $\mathrm{C_L}$ is the concentration of copper-complexing ligand, α' is the α-coefficient of $\mathrm{Cu^{2+}}$ with inorganic complexes and SA, and K'_{CuL} is the conditional stability constant of copper organic complex (CuL). In the presence of single ligand and using a linear least squares regression, the plot of $[Cu_{labile}]/[CuL]$ as a function of $[Cu_{labile}]$ is straight. However, the plot shows curvature in the presence of two or more ligands. Value for C_L was obtained by the slope^{-1} whereas K'_{CuL} was obtained from $K'_{CuL} = \alpha' \times \text{slope} / Y\text{-axis intercept}$. Further details of theory and data treatment can be obtained elsewhere (Campos and van den Berg 1994; Laglera and van den Berg 2003; Chapman et al. 2009).

Results and discussion

The impact of time on the release of DOC

During preliminary experiments, marine sediments were suspended in UV-irradiated seawater and the total and labile copper (labile copper is denoted for electrochemically active copper species) was measured in the samples. These experiments have indicated the potential release of copper-complexing ligands to seawater due to the presence of non-labile fraction of copper, calculated by the difference between the concentration of labile copper and total copper. The copper-complexing ligands are believed to be of organic nature rather than inorganic. The correlations between copper-complexing ligands and DOC were strong and positive in the water column of western North Atlantic (Zhou and Wangersky 1989). Therefore, DOC can be used to predict the release of organic ligands as function of time under the circumstances of our experiments. Along the interval time of 24 h, with suspension of various amounts of sediments in UV-irradiated seawater (free of organic ligands), the maximum concentration of DOC was observed after 4 h whereas after this time interval, the concentration of DOC showed more or less constant value or even decrease (Fig. 2). This interesting finding indicates that some of DOC is likely to re-adsorb on the sediment and/or degradation of certain amount of easily oxidized DOC occurred after 4 h. For this study and in order to investigate the potential releases of copper-complexing ligands from coastal sediments, an equilibration time of 24 h and suspension of 2 g of the sample in UV-irradiated seawater were used to study copper speciation. The use of 24 h was selected to ensure the stability of organic ligands released from the marine sediments while selection of 2 g of the sample was arbitrary.

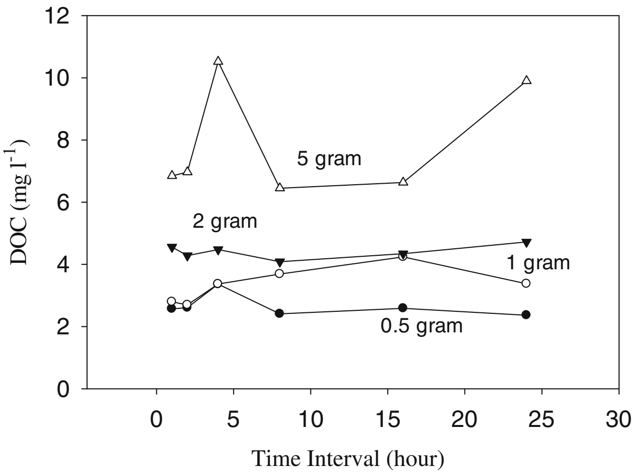

Fig. 2 The impact of time on the releases of DOC from suspended sediments in UV-irradiated seawater using 0.5, 1, 2, and 5 g of sediment

Sedimentary copper-complexing ligands and their conditional stability constants

The values of sedimentary copper-complexing ligands, conditional stability constants of copper with organic complexes, total copper, carbonate content, and organic carbon content in the coastal sediment of eastern Red Sea are shown in Table 1. The concentrations of copper-complexing ligands are reported as nanomolar per gram. Usually, concentrations of copper-complexing ligands in marine sediments for most studies are reported as nanomolar as these studies focus on the fluxes of copper-complexing ligands from porewater reservoir to the upper waters. Here, we assume that copper-complexing ligands are potentially released to the overlaying water by re-suspension of marine sediments under the impact of waves and currents. The titration of samples followed by linearization has indicated the presence of two ligands: a strong (L_1) and a weak ligand (L_2) (Fig. 3). The concentration of L_2 is significantly low at station HQ1 (8.33 nM g^{-1}) whereas the values are almost close to 25 nM g^{-1} at the other stations with highest value recorded at Reayat Al-Shabab Lagoon (28.35 nM g^{-1}). The concentrations of L_1 show similar pattern with lowest value at station HQ1 (3.53 nM g^{-1}) and highest value at Reayat Al-Shabab Lagoon (25.58 nM g^{-1}). However, the variability of L_1 values is evident in comparison to the values of L_2. This may indicate that L_1 is more sensitive to the environmental conditions or its production is enhanced by diagenetic processes in the sediments. In general, the value of L_2 is higher than the value of L_1 by a factor of 2–4. The only exceptional is observed at station RS3 as the value of L_2 (28.35 nM g^{-1}) is almost equal to the value of L_1 (25.58 nM g^{-1}). It is worthwhile to mention that the stability constants of the complexing ligands with copper from the present study are in good agreement with the stability constants obtained by Chapman et al. (2009)) for shallow lagoon waters. The authors have measured the concentrations of thiols and copper-complexing ligands (L_1 and L_2) and suggested, based on similarity of thiols and L_2 concentrations, that L_2 is dominated by thiols. It is therefore possible that thiols consist of major parts of L_2 in the coastal sediments of eastern Red Sea. For most studies on copper speciation in seawater, almost one ligand was found as inferred from linearization technique developed by van den berg (1982) and Ruzic (1982). L_1 seems to be more resistant to the

Table 1 Concentrations of sedimentary copper-complexing ligands ($[L_2]$ and $[L_1]$; nM g^{-1}), logarithm conditional stability constants (log K_2 and log K_1), total copper, organic carbon content, and carbonate content in the coastal sediments of eastern Red Sea

Station	$[L_2]$ (nM g^{-1})	Log K_2	$[L_1]$ (nM g^{-1})	Log K_1	Total copper (μg g^{-1})	Organic carbon content (%)	Carbonate content (%)
HQ1	8.33 ± 0.98	12.12 ± 0.01	3.53 ± 0.11	13.77 ± 0.20	8.33	0.053	25
NC2	24.90 ± 5.00	11.79 ± 0.01	6.60 ± 0.65	13.33 ± 0.18	6.25	0.291	89.97
RS3	28.35 ± 2.10	11.95 ± 0.00	25.58 ± 1.05	12.59 ± 0.40	74.75	2.244	66.445
AR4	26.40 ± 4.20	12.96 ± 0.01	13.65 ± 1.43	13.97 ± 0.01	121.67	3.631	35.998
SC5	21.83 ± 3.83	11.91 ± 0.01	6.98 ± 0.74	13.10 ± 0.17	11.67	0.77	63.9

oxidation, and/or its production is enhanced in situ by the activities of marine phytoplankton. The in situ production of L_1 was suggested as a result of metabolism processes by marine phytoplankton (Zhou and Wangersky 1989; Moffett and brand 1996; Croot et al. 2000). Based on the results from the present study and as copper concentrations in seawater are usually less than the concentrations of copper-complexing ligands (Al-Farawati, unpublished data), we suggest that L_1 could have substantial impact on the biogeochemical cycle of copper in the coastal waters of Red Sea compared to L_2. The importance of L_2 seems to appear in environments of high levels of copper such as polluted areas. Such speculations were also suggested in estuarine environments (Laglera and van den Berg 2003; Santos-Echeandia et al. 2008a). In addition, relatively high levels of copper and copper-complexing ligands were reported in estuarine waters and were attributed to resuspension of sediments (Santos-Echeandia et al. 2008a). However, in order to assess the impact of L_1 and L_2 on the biogeochemical cycle of copper in the Red Sea, the magnitude of the flux from the sediments has to be evaluated.

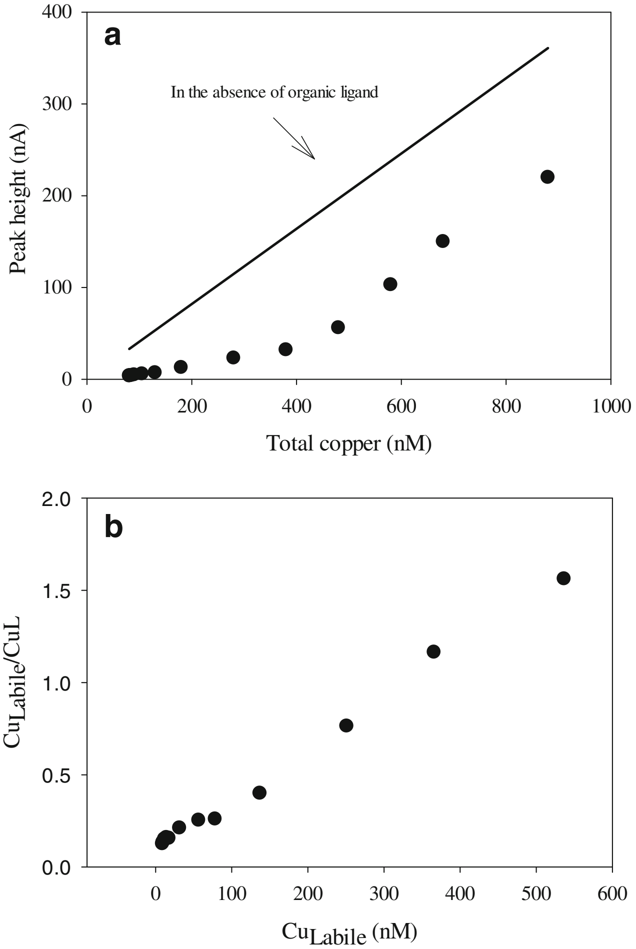

Fig. 3 Complexing ligand titration of filtrate after suspension of sediment from station RS3 in UV-irradiated seawater for 24 h (using 5 μM SA). **a** Peak height versus total dissolved copper; the *straight line* is for calculated peak height in the absence of organic ligands. **b** Linearization of the data showing curvature indicating the presence of two ligands

Correlation of complexation parameters with total copper, organic carbon content, and carbonate content

Correlations of complexation parameters (copper-complexing ligands) with total copper, organic carbon content, and carbonate content in the marine sediments of eastern Red Sea are shown in Fig. 4. A strong and negative correlation was reported between the organic carbon content and carbonate content in the sediments of Red Sea (Basaham 1998; El-Sayed et al. 2002; Basaham 2008). One would expect that the correlation of the complexing ligand concentrations with organic carbon content to be positive whereas the correlation with carbonate content is expected to be negative. The correlation pattern for the copper-complexing ligand L_2 with total copper and organic carbon content is identical showing positive correlation with an arch shape (Fig. 4a, b). The correlation for copper-complexing ligand L_1 with total copper and organic carbon content is also positive but with relatively linear relationship (Fig. 4c, d). Surprisingly, the correlation of copper-complexing ligands with carbonate contents has not show negative pattern as it would be expected (Fig. 4e, f). Total copper is strongly correlated to organic carbon content ($r^2 = 0.99$), and that could be attributed to the simultaneous precipitation with particulate materials (Fig. 4g). Copper is considered as scavenging type element that is removed from the water column due to adsorption on particulate materials and eventually buried in the sediments (Bruland 1983; Chester

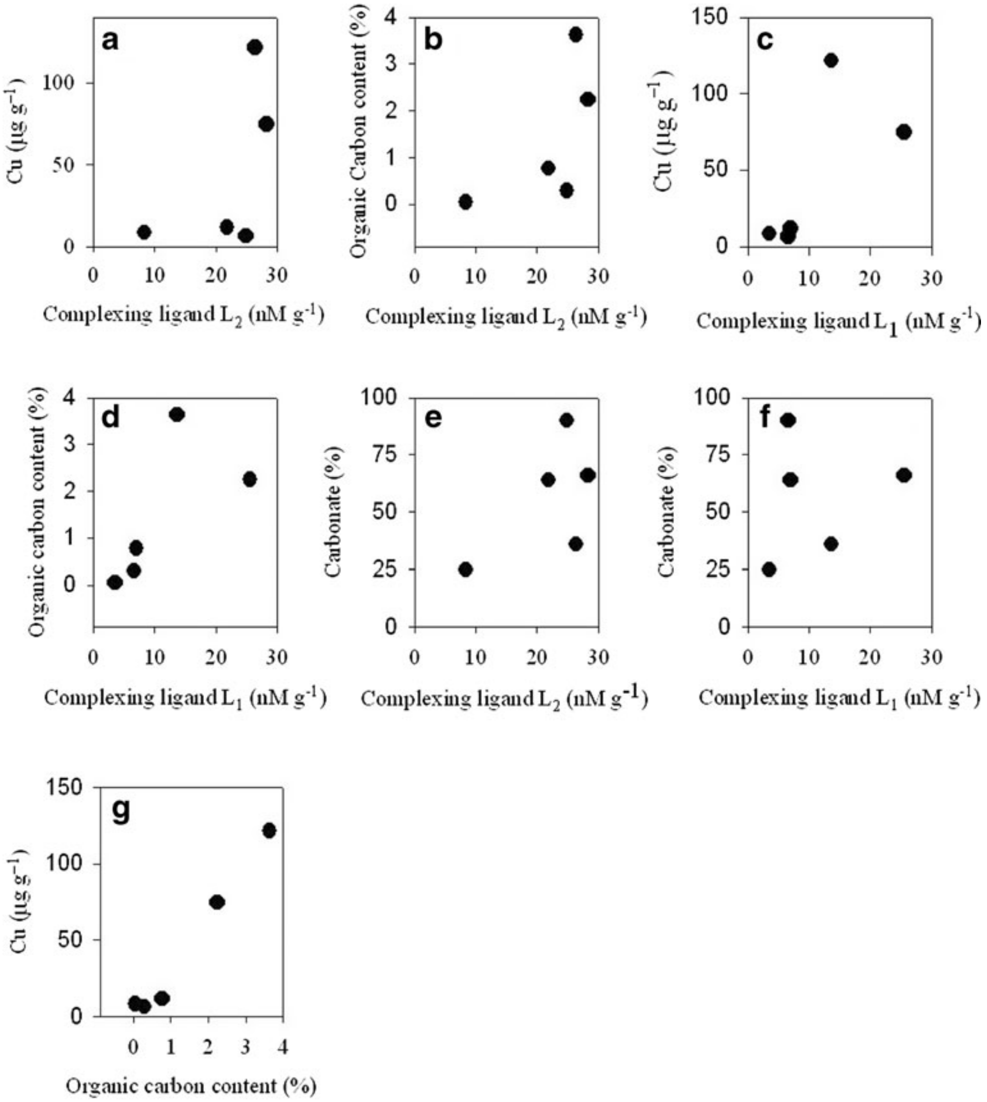

Fig. 4 Correlations of the concentrations of complexing ligands (L_1 and L_2) with total copper, carbonate content, and organic carbon content in the coastal sediments, eastern Red Sea

2003). Such behavior is reported in the coastal waters of Jeddah due to a strong and negative correlation that was found between dissolved copper and particulate organic materials (Al-Farawati et al. 2011). Additionally, copper is one of bio-limiting element nutrient that is utilized by the marine organisms. For example, the growth of the dinoflagellate *Gonyaulax tamarensis* was shown to be limited at cupric ion activities less than 10^{-13} M (Schenck 1984). After the death of marine organisms, copper accumulates in the sediments along with organic materials.

Potential impact of copper complexation data on dissolved copper

Dissolved copper speciation was investigated in coastal waters of Southern Corniche of Jeddah (Al-Farawati, unpublished data). The authors have modeled their data based on single complexing ligand, and they reported value of L_1 in the range between 5 and 133 nM whereas the log K_1 was in the range between 12.26 and 13.65. Using these values, the authors were able to calculate the concentration of free copper in seawater which was found to be in the range $10^{-12.79}$ to $10^{-15.08}$ M. Comparison of the values of log K_1 obtained in the sediments (the range; 12.59–13.97) with seawater values that have been observed by Al-Farawati (unpublished data) shows close agreement. In order to evaluate the importance of the copper-complexing ligands from sediment on the dissolved copper speciation, the fluxes of copper-complexing ligands have to be estimated. To evaluate the impact of marine sediments as a source of copper-complexing ligands to seawater, the resuspension of the sediments in the coastal waters of Jeddah for the Sothern Corniche area (St. SC5) is estimated based on a model using the wind data to estimate the resuspension of the sediments in shallow coastal waters (Booth et al. 2000). The model is based on wind-induced wave phenomenon developed by coastal engineering Research Center, US

Army Corps of engineering (SPM 1984). Furthermore, the grain size of the sediment is an important factor in the calculation of the flux. The grain size analysis of the sediment for the South Corniche shows that the sediment type is gravel sandy. For this study, it is assumed that the sea is fully developed. The wind data recorded at the Obhur Meteorological Station show that during April, the wind is mainly from N to NE. The Meteorological Station records various parameters at 15-min interval including the wind speed and direction. By utilizing the wind speed, direction, and grain size of the sediment, the resuspension of marine sediments in South Corniche area is estimated to be 361 g m^{-2} day^{-1}. Using values of 6.98 nM g^{-1} for L_1 and 21.83 nM g^{-1} for L_2 in the area of South Corniche (Table 1), the daily flux of L_1 and L_2 is accounted to 2.52 and 7.88 μM m^{-2} day^{-1}, respectively. The daily flux of L_1 in South Corniche is comparable with the value for non-vegetated area in Tagus estuary (2.16 μM m^{-2} day^{-1}, Santos-Echeandía et al. 2013) whereas the flux of L_2 in South Corniche is higher by 3–4 orders of magnitude (2.31 μM m^{-2} day^{-1} for Tagus estuary). However, the fluxes of L_1 and L_2 for vegetated area in Tagus estuary are 11.5 and 64.7 μM m^{-2} day^{-1}, respectively (Santos-Echeandía et al. 2013). These values exceed our values which indicate the importance of vegetation as a source of copper-complexing ligands in the marine environments. On the other hands, our values are higher by several orders of magnitude than the values reported for total the flux of copper-complexing ligands for Chesapeake Bay (0.3–1.2 μM m^{-2} day^{-1}, Skrabal, et al. 1997). On the basis of daily presence of dissolved copper-complexing ligands in South Corniche and using average value of 21.7 nM (Al-Farawati, unpublished data), the contribution of sedimentary copper-complexing ligands to the pool of dissolved copper-complexing ligands in the upper seawater layers represents less than 13 % that indicates the potential contribution of other sources such as in situ production (Croot et al. 2000) and sewage effluent (Santos-Echeandia et al. 2008b).

Conclusion

Marine sediments from the coastal environments of eastern Red Sea were suspended in UV-irradiated seawater. Detection of copper using ACSV in the filtrate revealed the presence of non-labile fraction of copper that is attributed to complexation of copper by organic ligands released from the sediments. Copper-complexing ligands and their conditional stability constants are determined by competition of SA and organic ligands for copper. Two classes of copper-complexing ligands are detected. Thiols are likely to contribute to the majority of the weaker ligand (L_2). The contribution of copper-complexing ligands from the sediments to the pool of dissolved copper-complexing ligands in the south coast of Jeddah is less than 13 %. This indicates that other sources have to be considered in order to evaluate their role in the biogeochemical cycle of copper in the coastal water of Red Sea.

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