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Physico-chemical forms of copper in water and sediments of Lake Pontchartrain basin, USA

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HIGHLIGHTS

- The Cu content in water and sediment in Lake Pontchartrainbas in were investigated.
- Cu partitioning in water decreased as inert > labile > organic indifferent seasons.
- Sediment acted as a source and sink of Cu influenced by season and temperature.

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ABSTRACT

In this study, one of the largest estuaries in the Gulf Coast of USA was investigated for Cu forms and fractionations. Both the water and sediment samples in subsegments of the Lake Pontchartrain basin were collected and Cu forms in dissolved phase and sediment phase were analyzed. The BCR sequential extraction procedure was used to extract Cu in exchangeable, reducible, oxidizable and residual fractions in sediments. The results showed that the residual fraction of Cu was a major contributor in Tangipahoa River and I-10 Bridge sediments, while the residual and oxidizable fractions in the case of oil refinery sediments. Cu partitioning in Lake Pontchartrain basin water showed the decreasing trend of inert > labile > organic in both spring and summer. The release of Cu from the sediments into the water column was greater in summer as compared to spring and vice versa. Lower temperature helps in the adsorption of Cu on the surface of sediments in early spring due to low disturbance and temperature.

1. Introduction

Lake Pontchartrain is the second-largest brackish estuary located in southeastern Louisiana, United States. It covers an area of 1630 km^2 with a mean depth of 4.0 m (DeLaune et al., 2009). The estuary drains the Pontchartrain Basin, over an area of 12,000 km^2 situated on the eastern side of the Mississippi River delta plain. Lake Pontchartrain has served the surrounding communities for >1000 years. Estuarine and coastal areas are the key important sites for human inhabitants, supports fishing, swimming, boating, crabbing and other recreational activities (McKinley et al., 2011). The Lake Basin is Louisiana's premier urban estuary and nearly one-third of the state population live in this area. However, with rapid urban and industrial development, heavy metals (HMs) are transported to the estuarine and coastal sediments from upstream areas of the catchment (Muniz et al., 2004; Xia et al., 2011). Over the past decades, human activities associated with municipal discharge of pollutants, surface drainage, land runoff, rapid growth and development within the Pontchartrain basin have resulted in a significant environmental degradation, affecting the water quality and loss of critical habitat in and around the Lake (Penland et al., 2002; Flocks et al., 2009; Zhang et al., 2016a).

The natural sediment source is through drainage from smaller associated rivers, bayous, and shoreline erosion. The high rates of bioturbation and resuspension of the bottom sediments make the accumulation rates very difficult to determine (Flocks et al., 2009; Penland et al., 1997). HMs contamination in sediment affects water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Fernandes et al., 2007; Abdel-Baki et al., 2011). In most

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cases, the major part of the anthropogenic metal contribution in water bodies and sediments has a terrestrial source, added by mining and industrial installations along rivers and estuaries system (Ridgway et al., 2003; Caeiro et al., 2005; Sundaray et al., 2011).

Quantification of the land-derived metal fluxes is, therefore, a key factor to find out the extent of HMs inputs influencing the biogeochemical processes of the HMs in the marine system (IGBP, 1995; Cobelo-Garcia et al., 2004). The spatial distribution of HMs in water and sediments is vital to draw out their contribution in aquatic systems and identifying the possible sources of contamination (Birch et al., 2001; Rubio et al., 2001).

Copper (Cu) is one of the important essential nutrient elements for aquatic organisms (Zhang et al., 2016a). In fact, copper is a common ingredient in many algaecides and herbicides (Jancula and Marsalek, 2011). Therefore, understanding the mechanisms of accumulation and geochemical distribution of Cu in water and sediments is fundamental for the management of the coastal environment. Cu exists in a variety of physicochemical forms or fractions in aquatic systems. It is well established that Cu exerts toxic effects on aquatic species ranging from bacteria and plants to fish and benthic invertebrates (Campana et al., 2012). Furthermore, the free or soluble ion is the most bioavailable and toxic form of Cu (Luider et al., 2004; Brooks et al., 2007). Dissolved Cu is generally controlled by sediment phase Cu and not all species of Cu are bioavailable to aquatic organisms. Dissolved Cu as low as 40 $\mu g\,L^{-1}$ has been found to be toxic to many fish (Erickson et al., 1996), at 3 $\mu g\,L^{-1}$ has been shown to cause toxicity to *coho salmon* (Scholz et al., 2003). Clearly understanding the dominance of bioavailable fraction of Cu and its speciation is important for risk assessment of Cu in aquatic ecosystems.

The speciation of dissolved Cu controls its bioavailability as well as its geochemical cycling. The influence of acid-volatile sulfides (AVS) and sediment particle size on metal bioavailability are well understood (Simpson et al., 2011). In coastal waters, the total dissolved Cu concentrations are typically higher than background Cu levels, as a consequence of organic complexation (Sundaray et al., 2011; Kozelka and Bruland, 1998; Shank et al., 2004). Hence, this is the first investigation about the higher Cu content in both water and sediments in the Lake Pontchartrain basin and associated river in the different time intervals. This can provide a new insight into the Cu contribution from different rivers in the Lake as well as its effect of different speciation on Lake biota.

Therefore, present study was aimed to identify the sources of Cu in Lake Pontchartrain basin, its fractionation in water and sediments, potential effects on Lake biota and better management of the water resource of Lake Pontchartrain basin.

2. Materials and methods

2.1. Water sampling and pretreatment

Lake Pontchartrain is an oval-shaped quasi-enclosed water body. The lake east-west and north-south axis span are 66 and 40 km, respectively (DeLaune et al., 2009). The lake is connected to the Gulf of Mexico via Rigolets strait, to Lake Borgne via Chef Menteur Pass, and to Lake Maurepas via Pass Manchac. These lakes form one of the largest estuaries in the world. Lake Pontchartrain receives fresh water from many rivers located in the north and north-west. Nine sampling sites were chosen representing the Mississippi River, Amite River, Tickfaw River, Tangipahoa River, Tchefuncta River, Lacombe Bayou, Liberty Bayou, Blind River and Industrial Canal around the Lake Pontchartrain in Louisiana, USA. These sites represent the water bodies discharged into the Lake Pontchartrain Basin. The nine sampling locations are shown in Fig. 1. The water samples were collected on February 10th and June 9th, 2009, which represent the spring and the summer samples, respectively. Ten water samples (T1-T10) from shore to mid of Lake Pontchartrain (Fig. 1) were collected at same locations on 10th October 2008 and 23rd April 2009, denoting autumn and spring, respectively. The water and sediments samples were collected from I-10 bridge over the Lake Pontchartrain (Fig. 1) on 19th February 2009 and 16th July 2009, representing spring and summer, respectively. Oil refinery (functional since the 1920s) sediments samples were collected on 12th July 2009 (Fig. 1). Tangipahoa River water and sediments samples were collected on 9th July 2009 (Fig. 1). All water samples were collected using a plastic dipper and stored in two 1000 mL polypropylene bottles. All water samples were stored in an insulated cooler containing ice and delivered to the laboratory on the same day and kept at 4 °C until processing and analysis. For the water samples, one bottle was used for Cu partition analysis, another one for dissolved Cu analysis. All the glass wares and polyethylene bottles were cleaned by soaking in hot 50% nitric acid for more than 3 days before use (Ahlers et al., 1990).

2.2. Water analysis

2.2.1. Dissolved Cu and partitioning analysis in water samples

The water samples were passed through 0.45 μm pore size membrane filter to determine dissolved Cu in the water samples. The dissolved Cu was analyzed by a Perkin-Elmer Sciex Elan 9000 ICP-MS after HNO_3 acidification. The total dissolved Cu in the Lake Ponchartrain water was showed in Table 1, and the total Cu concentration in the Lake Ponchartrain basin river waters and sediments (Mississippi river, Amite river, Tickfaw river, Tangipahoa river, Tchefuncta river, Lacombe bayou, Liberty bayou, Blind river and Industrial canal) was indicated in Zhang et al. (2016a, 2015a); while the total Cu concentration in the Lake Ponchartrain I10 Bridge waters and sediments was given in Zhang et al. (2016b), and the total Cu content in the sediment near the oil refinery was showed in Zhang et al. (2015b).

The labile and organic fractions in soluble phase of the water samples were analyzed by a fractionation process using resin column (Jiann and Presley, 2002), and the specific process is shown in Zhang et al. (2016a). Approximately 2.0 g Chelex-100 (Analytical Grade, 100–200 mesh, Sodium form) and 1.0 g AG MP-1 (Analytical Grade, 100–200 mesh, Chloride form), were separately filled into Poly-Prep columns (Bio-Rad) in 2 N HNO_3. Resins were transformed to NH_4^+ and OH^- forms, respectively, by washing the columns with 10 mL of 1 M NH_4OH solution. After rinsing with deionized water, the columns were connected with the Chelex-100 column on top and the AG MP-1 column on the bottom. The water samples were passed through the column system and the flow rates were adjusted at 2–3 $mL\,min^{-1}$ using a two-way stopcock. The contact time was maintained at 10–20s. When the water samples had been passed through the column systems, the columns were disconnected and rinsed with deionized water (2 × 5 mL), followed by 1 M ammonium acetate (5 × 4 mL) at pH 5.5 to separate the major ions from the Cu. After the major ions (Na, Ca, Mg, K) were isolated from the Cu element in the resin columns, followed by washing with deionized water, Cu was eluted by 7 mL of 2 N HNO_3. The process led to the enrichment factor of up to 150 with a 1000 mL sample. The column volume was 4.0 mL (ID 7 mm, length 10 cm) for Chelex-100, and 1.56 mL (ID 7 mm, length 4 cm) for AG MP-1. The forms of Cu separated by this procedure were defined as labile (Chelex-100), organic (AG MP-1), and inert forms (colloidal metals) in our previous published paper (Zhang et al., 2016a). The eluent was analyzed by Perkin-Elmer Sciex Elan 9000 ICP-MS.