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Sediment amino acids as indicators of anthropogenic activities and potential environmental risk in Erhai Lake, Southwest China

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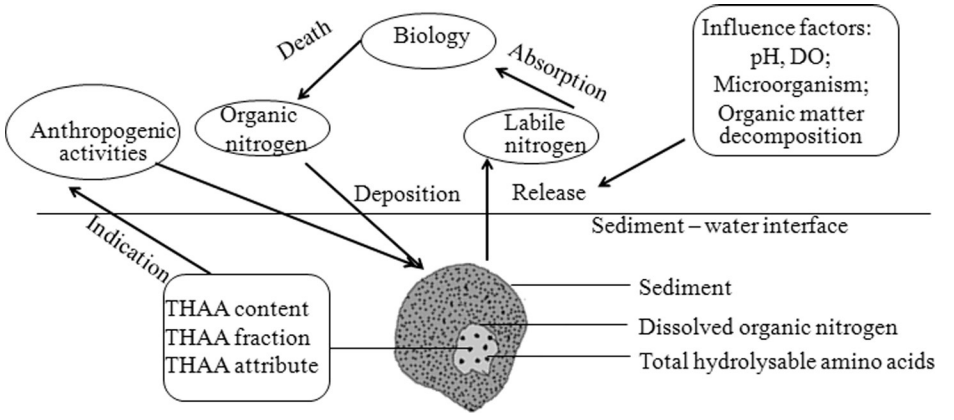
HIGHLIGHTS

- Relationship between sediment THAAs and anthropogenic activities and lake environment.
- Potential sediment THAA release based on changes in environmental conditions.
- Sediment THAA could effective reflects anthropogenic activities and aquatic environmental characteristics.
- Sediment THAA is important to influence lake water quality.

GRAPHICAL ABSTRACT



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ABSTRACT

Total hydrolysable amino acids (THAAs) constitute the most important fraction of labile nitrogen. Anthropogenic activities directly influence various biogeochemical cycles and then accelerate lake ecosystem deterioration. This is the first study that has established the relationship between sediment THAAs and anthropogenic activities using dated sediment cores, and evaluated the possibility of THAAs release at the sediment interface based on changes in environmental conditions in Erhai Lake. The results showed that historical distribution and fractions of THAAs could be divided into three stages: a stable period before the 1970s, a clear increasing period from the 1970s to 1990s, and a gradually steady period that started after the 1990s. The chemical fraction, aromatic and sulfur amino acids (AAs) accounted for only ≤3% of THAAs. Basic AAs accounted for 5–17% of THAAs, and remained at a relatively stable level. However, acidic and neutral AAs, which accounted for 19–44% and 35–69% of THAAs, respectively, were the predominant factors causing THAAs to increase due to rapid agricultural intensification and intensification of contemporary sedimentation of phytoplankton or macrophytes since the 1970s. These trends were closely related to both anthropogenic activities and natural processes, which implied that sediment THAAs could act as an effective indicator that reflects anthropogenic activities and aquatic environmental characteristics. The current contributions of sediment THAAs on TN and TOC were <5% and 1.5%, respectively. However, the dramatic increase in THAAs in the sediment cores indicated that there was a huge potential

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source of labile nitrogen for the overlying water under certain environmental conditions. Correlation analysis suggested that the release of THAAs was negatively correlated with pH, whereas positively correlated with bacterial number and degree of OM mineralization, which particularly depend on the stability of HFOM. Therefore, the risk of sediment THAAs release might increase when the sediment environment continuously changes.

1. Introduction

Dissolved organic nitrogen (DON) has been recognized as an important component of fixed nitrogen (N) in aquatic ecosystems and plays an important role in phytoplankton growth and eutrophication status (Lu et al., 2014; Berman and Bronk, 2003). Amino acids (AAs), the building blocks of proteins, are the predominant component of DON in both terrestrial and marine organisms (Fernandes et al., 2014). Total hydrolysable amino acids (THAAs) and its components serve essential functions in lake ecosystems because these could be released into the overlying water and be utilized as an important N and carbon source for phytoplankton and microorganism growth (Stepanauskas et al., 1999). Evidence has suggested that THAAs account for only a small proportion of the total DON pool, but these significantly contribute to the DON flux in aquatic ecosystems (Tada et al., 1998; Lu et al., 2014). Therefore, the role of THAAs in aquatic ecosystems has recently become an important research topic (Fernandes et al., 2014; Gupta and Kawahata, 2000). Previous studies have partly proven that THAAs properties, including content, forms, and their availability could be utilized as an effective tool that could identify the source, decomposition, and remineralization of organic matter (OM) and N (Pantoja and Lee, 2003; Cowie et al., 1992; Dauwe and Middelburg, 1998; Thomas and Eaton, 1996; Zhao et al., 2013a).

Sediments are the major repository of THAAs and play an important role in biogeochemical cycles that occur in lake ecosystems (Bourgoin and Tremblay, 2010). On one hand, sediments are an important sink: THAAs are adsorbed on suspended particulates that eventually reach the lake floor and are continuously covered by successive sediment layers (Ni and Wang, 2015), indicating that the record of temporal variations in THAAs in sediments directly reflects the natural and anthropogenic activities over time. However, our understanding of the relationship between THAAs characteristics and environmental dynamics as well as anthropogenic activities in a specific aquatic ecosystem is limited. Therefore, detailed information on THAAs characteristics relative to environmental dynamics and anthropogenic activities is important in guiding anthropogenic production and life style, as well as in protecting the aquatic ecological environment. On the other hand, sediments also act as a potential source of THAAs that are released into the overlying water as sedimentary environmental conditions change. Hence, elucidating the effect of environmental parameters on the potential release of THAAs at the sediment interface is important in controlling water quality and preventing the occurrence of algae blooms.

Erhai Lake is the second largest freshwater lake in Yunnan Province, which is located in the southwest region of China. This region plays a crucial role in local socioeconomic development as a source for irrigation, drinking water, tourism, and fisheries. Monitoring data have shown that the mean concentrations of total nitrogen (TN), dissolved TN, and DON in water in 2013 were approximately 0.57 ± 0.06, 0.41 ± 0.02, and 0.15 ± 0.03 $mg \cdot L^{-1}$, respectively (Wang et al., 2015). The water quality has been graded to be of classes II to III, which is mainly based on the overlying water environment quality standard (GB3838-2002) of China (Wang et al., 2012a). However, the contents of TN, dissolved TN, DON, and OM in sediments were much higher than most eutrophicated lakes in China (Wang et al., 2015), reaching 4207 ± 1867, 89 ± 19, 27 ± 9 $mg \cdot kg^{-1}$, and 5.2%, respectively. THAAs are the major component of labile DON in the sediments of Erhai Lake, and accounts for approximately 31% of DON (Zhang, 2015). These large amounts of THAAs represent a massive reservoir for N and C that is released to the overlying water under certain geochemical environments. Unfortunately, its environmental conditions (including pH, microorganisms and OM mineralization) have continuously changed over the past decades (Wang et al., 2015), thus increasing the risk for THAAs release from sediments. On the other hand, due to agricultural intensification in the upper area of the watershed since the 1970s, the ecosystems of Erhai Lake have severely deteriorated and its water quality has changed from mesotrophic to eutrophic (Zhao et al., 2013b). Therefore, the effect of the endogenous labile N (THAAs) on the water quality of Erhai Lake should be extensively evaluated. Accordingly, the main objectives of the present study were as follows: (1) to establish the relationship between anthropogenic activities and changes in THAAs using dated sediment cores, and (2) to evaluate the potential risk for surface sediment THAAs release based on changes in environmental conditions (e.g., pH, microorganisms and OM mineralization) of Erhai Lake.

2. Materials and methods

2.1. Study area

Erhai Lake is located in Dali City, Yunnan Province, with a surface area of approximately 249 km^2 and a watershed area of 2,565 km^2. The lake has a mean depth of 10.5 m and a volume of 2.8×10^9 m^3 (Fig. 1). As one of the typical agricultural regional lakes in the Yunnan-Guizhou Plateau of China, exogenous N is primarily derived from agriculture by river and ditch from the northern and western areas such as farmland, aquaculture, and livestock, particularly due to the extensive use of artificial N fertilizers in the upper area of the watershed. The rapid intensification of agricultural activities in the last few years, especially since the opening of agriculture jobs in the late 1970s, has resulted in a significant deterioration of the lake's ecosystem and water quality (Ni et al., 2011). Therefore, to select the Erhai Lake as a case study area was critical and necessary.

2.2. Sample collection

2.2.1. Surface sediments

Ten surface sediments (0–5 cm) from Erhai Lake were collected using a core sampler (HL-CN, Xihuayi Technology, Beijing, China) in October 2012, which was a high-risk period for algal blooms and decline in water quality. Samples were selected from the northern (E1, E2, E3, and E4), central (E5, E6, and E7), and southern (E8, E9, and E10) areas of the lake, which was based on the topography of the lake bottom (Li et al., 1999). These areas were assumed to represent the entire lake based on the overall characteristics of different regions and to reflect the true situation of Erhai Lake.

2.2.2. Core sediments

Three sediment cores (E1, E6, and E8) were collected from different areas of Erhai Lake in October 2012. Core E1 (northern site: 100°09′13″E, 25°54′00″N) is located at the lower edge of the alluvial fan of the Yongan River, a major inflow river. Water exchange is this particular region occurs at a faster rate relative to that of other areas. The area has no aquatic plant growth due to severe agricultural non-point source pollution and livestock manure. Core E6 (central site: 100°11′49″E, 25°47′59″N) is located at the deepest region (21.1 m)