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Using multiple combined analytical techniques to characterize water extractable organic nitrogen from Lake Erhai sediment

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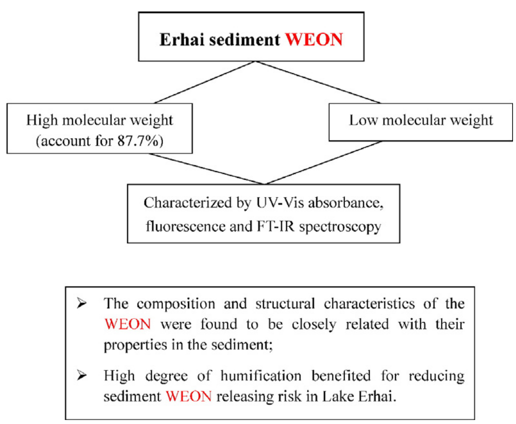
HIGHLIGHTS

- Multiple methods were used to characterize the WEON in Lake Erhai sediment.
- Erhai sediment WEON comprised predominantly high molecular weight WEON species.
- Abundant humic substances aliphatic compounds, stable to biodegradation.
- $P_{III+V,n}/P_{I+II+IV,n}$ was taken as an indicator for WEON content in Erhai sediments.
- The composition and structure of the WEON affect the sediment properties.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, UV–vis absorbance, fluorescence, and FT-IR spectroscopy were combined to characterize the components and structure of the water extractable organic nitrogen (WEON) in Lake Erhai sediment. Lake Erhai sediment WEON comprised predominantly high molecular weight WEON, with the fraction with a molecular weight > 1 kDa accounting for 87.7% of the total. It was mainly composed of humic acid-like substances, with fewer simple aromatic proteins. Large amounts of aliphatic and amide compounds were detected by IR in the sediments. There were more polymerizable aromatic rings and carbonyl, carboxyl, hydroxyl, and ester compounds in the high molecular weight WEON than in the low molecular weight WEON. Additionally, fluorescence regional integration results implied that the ratio $P_{III+V,n}/P_{I+II+IV,n}$ can be indirectly taken as an indicator for WEON content in Erhai sediments. Furthermore, the composition and structural characteristics of the WEON were found to be closely related with their properties in the sediment. The large amount of aliphatic compounds in the sediment as well as the relatively high humification and aromatic degree in high molecular weight WEON, stabilizes the WEON in Lake Erhai sediment. Compared with other lake sediments of different trophic statues (such as Lake

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Dianchi, Lake Poyang, Lake Taihu and Lake Donghu), Erhai sediment exhibited a higher degree of humification, which benefited for reducing sediment WEON releasing risk. And it can be regarded as the reason why the nutrient content in Erhai sediment is very high, but its water quality is still good.

1. Introduction

Dissolved organic nitrogen constitutes the largest part (20% to >90%) of the total dissolved nitrogen (TDN) in aquatic systems such as lakes, rivers, estuaries, and surface ocean waters (Worsfold et al., 2008). It was conventionally believed to be composed mainly of refractory compounds resistant to biological degradation and generally unavailable as sources of nutrition for phytoplankton or bacteria (Berman and Bronk, 2003). However, in recent years, researchers have verified that 10–70% of dissolved organic nitrogen can be considered bioavailable (Seitzinger et al., 2002; Wiegner et al., 2006; Watanabe et al., 2014).

Water extractable organic nitrogen (WEON) is the organic nitrogen that can be extracted by water, salt solution, or electro-ultra-filtration (EUF) (Murphy et al., 2000). It includes both organic nitrogen in the pore waters and that attached on solid sediment surfaces. Dissolved organic nitrogen (DON) refers to nitrogen in the surface waters and in the pore waters of the sediments. As an important fraction of reactive nitrogen in freshwater lake ecosystems, WEON and DON are likely to enhance the production of greenhouse and ozone-depleting gases, such as N_2O (Badr et al., 2008). In addition, it may cause the diminution of dissolved oxygen, overgrowth of phytoplankton and, consequently, harm to aquatic animals (Fang et al., 2010; Wadhawan et al., 2014). Consequently, extensive studies on DON and WEON bioavailability in river, marine, and freshwater systems have been performed in recent decades (Seitzinger et al., 2002; Wiegner and Seitzinger, 2004; Cory and Kaplan, 2012; Xia et al., 2013).

WEON is a dynamic participant in the nitrogen cycle in aquatic systems (Berman and Bronk, 2003), and variations in the bioavailability of WEON are attributed, at least in part, to its composition and structure. DON is extremely complex, and available methods can identify only 30% of this nitrogen (Pehlivanoglu and Sedlak, 2006). Previous studies have attempted to characterize DON and WEON by various methods. Excitation–emission matrix (EEM) fluorescence spectroscopy can provide an overall view of fluorescent properties, and has been widely employed in structural identification and stability assessment (Yu et al., 2010). Pehlivanoglu and Sedlak (2006) reported that fluorescence spectra can be used to detect the unidentifiable DON because some of it is incorporated into humic substances. Fourier Transform Infrared (FTIR) spectra can be utilized to characterize the leachate-derived DON and provide considerable information on functional groups containing nitrogen (He et al., 2015). Katye et al. (2009) and Rajaa et al. (2015) applied Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to molecular level studies on rainwater- and river-derived DON. Also, sediment release has been shown to be an important source of WEON (Xia et al., 2013). Understanding the structure and compositional characteristics of WEON in sediment is thus key to the provision of better estimates of WEON dynamics in lake ecosystems and its influence on ecosystem function and water quality. However, only very limited information can be acquired concerning the structure and compositional characteristics of sediment WEON.

Lake Erhai is the second-largest fault lake in Yunnan Province, China. At present, Lake Erhai is in the initial stage of eutrophication. Compared with other ecosystems (Table 1), such as terrestrial ecosystems, wastewater treatment plant (WWTP) effluent, wet deposition ecosystems, or estuary ecosystems, the WEON to TDN ratio in lake sediments is relatively high (39 ± 10.5%). Compared with heavily polluted or hypereutrophicated lakes, such as Lake Datong, Lake Dong, South Lake (in the middle and lower reaches of Yangtze River), and Lake Dianchi, the WEON content in Lake Erhai sediment is lower. However, the sediment WEON/TDN ratio is similar to that of Lake Poyang and Lake Dongting sediments (ca. 40.52%) (Table 2), where the TP and TN contents of the overlying water of the two lakes are 29.0×10^{-4} mmol/L and 7.71×10^{-2} mmol/L, and 38.7×10^{-4} mmol/L and 8.07×10^{-2} mmol/L, respectively (Zhang et al., 2013). This illustrates that the WEON plays a vital role in the nitrogen cycle in the Lake Erhai ecosystem.

Elucidating the chemical composition of sediment WEON is therefore essential to understanding the fate of WEON, and is beneficial for assessing its responses to biogeochemical processes. Additionally, one technique alone is not adequate to characterize the WEON structure comprehensively. Therefore, in this study, UV–vis absorbance, 3-dimensional fluorescence excitation–emission matrix (3DEEM) spectroscopy, and FT-IR spectroscopy were utilized to explore the structure and compositional characteristics of Lake Erhai sediment WEON. Furthermore, the influence of WEON structure on the properties of Lake Erhai sediment was investigated.

2. Materials and methods

2.1. Brief introduction to study site

Lake Erhai lies at a latitude of about 1974 m, has a surface area of 251 km^2, and an average water depth of 10.5 m. Compared with other lake ecosystems (such as Lake Donghu, Lake Poyang, Lake Taihu and Lake Dianchi, S.I-1 and S.I-2), Lake Erhai is characterized by a high sediment nutrient content, with TP and TN concentrations of ca. 0.0973% and 0.4558%, respectively, but relatively clean water, with TP and TN

Table 1
Comparison of WEON (or DON) and WEON (or DON)/TDN ratios in different ecosystems.

Ecosystems	Sampling positions	WEON (or DON) ($\times 10^{-4}$%)	WEON (or DON)/TDN (%)	References
Terrestrial ecosystems	Dry-land farming system, Texas (Tillage)	1188.3	35.3	Carrillo-Gonzalez et al., 2013
	Dry-land farming system, Texas (cropping)	9.2	0.29	
Effluent of WWTP	Fargo WWTF, USA	3.8 ± 0.8	12 ± 2	Simsek et al., 2013
	Moorhead WWTF, USA	5.5 ± 0.5	15 ± 1	
Wet deposition	Southern margin of East China Sea	59.1 ± 32.3 μM	37 ± 5	Chen et al., 2015
	Northeastern United States	34 ± 4 μM	25 ± 5	Katye et al., 2009
Estuary	Plym Estuary, England	–	36 ± 17	El-Sayed et al., 2008
Lake sediment	Middle and lower reaches of Yangtze River (hypereutrophication)	200.6 ± 91.7	57.69	Lin et al., 2009
	Middle and lower reaches of Yangtze River (mesotrophication)	58.9 ± 41.6	40.52	
	Dianchi Lake sediment (eutrophication)	1.6–247.68	3.7–33.4	This study
	Erhai Lake sediment (initial stage of eutrophication)	37.2 ± 13.7	39 ± 10.5	This study