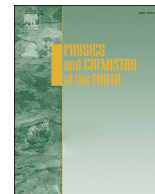




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Assessment of the content, structure, and source of soil dissolved organic matter in the coastal wetlands of Jiaozhou Bay, China

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ABSTRACT

The contents and the spectral analysis of dissolved organic matter (DOM) in four typical wetlands, such as naked tidal, suaeda salsa, reed and spartina, were conducted to investigate the content, structure, and source of DOM in coastal wetland soil. The soil samples were obtained from Jiaozhou Bay in January, April, July, and October of 2014. Results showed that the DOM contents in soil of four typical wetland were in order of spartina wetland > naked tidal > suaeda salsa wetland > reed wetland in horizontal direction, and decreased with the increase of soil depth on vertical section. In addition, the DOM contents changed with the seasons, in order of spring > summer > autumn > winter. The structural characteristics of DOM in Jiaozhou Bay wetland, such as aromaticity, hydrophobicity, molecular weight, polymerization degree of benzene ring carbon frame structure and so on were in order of spartina wetland > naked tidal > suaeda salsa wetland > reed wetland in the horizontal direction. On the vertical direction, they showed a decreasing trend with the increase of soil depth. The results of three dimensional fluorescence spectra and fluorescence spectrum parameters (FI, HIX, and BIX) indicated that the DOM in Jiaozhou Bay was mainly derived from the biological activities. The contents and structure of DOM had certain relevance, but the contents and source as well as the structure and source of DOM had no significant correlation. The external pollution including domestic sewage, industrial wastewater, and aquaculture sewage affected the correlation among the content, structure and source of DOM by influencing the percentage of non-fluorescent substance in DOM and disturbing the determination of protein-like fluorescence.

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1. Introduction

Soil dissolved organic matter (DOM) extracted using water or dilute salt solution 0.45 μm membrane is mainly made of the soil dissolved organic carbon (DOC), as well as dissolved organic nitrogen, dissolved organic phosphorus and dissolved organic sulfur (Wang et al., 2010). The content of DOM in soil was generally very low, but it was one of the most active components in the soil ecological environment. DOM had evident effects on the toxicity of pollutants (heavy metals, polycyclic aromatic hydrocarbons, pesticides, etc.) and the biochemical cycling of nutrient elements (C, N, S, P, etc.) (Lan et al., 2011; Bai et al., 2015), and was an important factor

affecting mineral weathering and soil formation process, the growth of microorganisms, and the transformation and decomposition of soil organic matter. At present, the research on soil DOM had covered biology, ecology, soil science, environmental science, and many other fields.

The farmland, forest, wetland, and other ecological systems had been involved in the study on soil DOM at home and abroad. The results showed that different soil ecological system had various DOM content, which was no more than 100 mgC/kg in farmland, usually 10–500 mgC/kg in wetlands (Wang et al., 2015a,b), and had large variation in forest ecosystem ranging from several to several hundred C mg/kg (Jiao and Li, 2005). The content of soil DOM in different ecological systems varied in horizontal direction, but decreased with the increase of soil depth on vertical section under the influence of hydrology and surface litter, soil microorganisms and human activities (Kong et al., 2013a,b; Wang et al., 2012). The previous studies on the degradation of soil DOM mainly focused on the degradation process of DOM and its influencing factors,

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suggesting that the degradation rate of DOM decreased with the increase of soil depth (Qualls and Haines, 1992). The degradation rate of DOM in different ecosystem was different, and the degradation rate of DOM in farmland soil was generally higher than that in forest soil (Boyer and Groffman, 1996). The internal properties of DOM, soil properties, and environmental conditions (vegetation, land use types, seasonal variation etc.) were the main factors affecting the degradation of soil DOM. The CO₂, CH₄ and other greenhouse gas produced during the degradation of DOM exerted a certain impact on global climate change (Kalbitz et al., 2000). As a carrier of pollutants, organic ligands of heavy metal, DOM contained carboxyl, hydroxyl, methoxy, and other active functional groups. The morphology and transformation of DOM in soil were affected because of his reaction with the metal ions, oxide and organic compounds in the soil through a series of reaction such as ion exchange, adsorption, complexation, chelating, flocculation, and redox process (Li and Qu, 2004). The previous studies mainly focused on the content, characteristics, distribution (Zhao et al., 2015), and the decomposition feature of DOM (Li et al., 2013a,b), as well as the interaction with soil nutrient elements (Carswell et al., 2016), heavy metal (Wang et al., 2004), and pollutant (Nelson et al., 1998). The different source of DOM inevitably affected its distribution characteristics and structural properties, and further influenced the degradation process and the interaction with soil components, which ultimately affected the biogeochemical processes of DOM in wetland ecosystem.

Wetland is a unique ecosystem in the water-land transition zone. Although the global wetland area only accounted for 4–5% of the total land area, but its carbon stocks accounted for 12–20% of the global terrestrial carbon reservoir (Liao et al., 2013). Soil DOM had become a research hotspot in wetland ecological system due to its fast moving, unstable, easily oxidized, and easily mineralizable characteristics. Many researches about soil DOM in wetland mainly concentrated in the Sanjiang plain, the Yangtze River Estuary, Hangzhou Bay, North Jiangsu tide beach wetland area (Wang et al., 2012, 2015a,b; Kong et al., 2013a,b; Yang et al., 2011; Bai et al., 2013), focusing on content and distribution of soil DOM under different vegetation and land use types, on soil DOM leaching, and the interaction of other ingredients in soil and so on.

The wetland was located in the water-land transition zone, where the hydrology changed sharply, material exchanged frequently, and DOM had various sources and different structure. It might have important scientific significance for the research of the content, source, and structure of DOM to reveal of wetland carbon budget, source sink change, formation mechanism and main characteristics of soil DOM in wetland ecosystem. However, little research has been done on the analysis of DOM source, especially the relation among the source, content, and structure characteristics of DOM.

At present, there are many methods used to analyze the structure and source of DOM, such as infrared spectrum, nuclear magnetic resonance, GC-MS, UV-Vis absorption spectrum, traditional fluorescence spectrum analysis, synchronous fluorescence spectroscopy and three-dimensional fluorescence spectroscopy (Mcdowell, 2003). Compared with other methods, three-dimensional fluorescence spectroscopy and UV-Vis spectroscopy are relatively simple characterization technologies of DOM, which have the advantages of high sensitivity, less consumption, no damage to the sample structure and other characteristics. In addition, three-dimensional fluorescence spectroscopy can qualitatively and quantitatively analyze the DOM.

In china, three-dimensional fluorescence spectra and UV-Vis spectral parameters analyses were mainly used on marine (Song et al., 2010), lake (Helms et al., 2013), estuary (Huang et al., 2013), reservoir (Guo et al., 2011). Some researchers also used them to

analyze the composition and structure of DOM in forest (Bi et al., 2013), farmland (Li et al., 2013a,b), and sediment (Wang et al., 2014), and the transformation and transport of DOM. However, few studies have been conducted on wetland, especially on coastal wetland.

The coastal wetland in Jiaozhou Bay is located in the coast of Jiaozhou Bay, which is the largest estuary wetland of Shandong peninsula and has been included in “the list of wetlands of china”. This study took the coastal wetland in Jiaozhou Bay as the object to illustrate the relation among the source, content, and structure characteristics of soil DOM. The results could provide a theoretical base to reveal the role of DOM in biogeochemistry cycle in coastal wetland, the basic data for researching and evaluating ecological functions of coastal wetland, and scientific guidance and technical support for the sustainable utilization and protection of wetland.

2. Materials and methods

2.1. Overview of the study area

Jiaozhou Bay wetland with the total area of about 17.76×10^4 hm² is mainly located in the northern and northwest coast of Jiaozhou Bay. According to the meteorological data of Qingdao city in the last hundred years, Jiaozhou Bay wetland belongs to the warm temperate monsoon climate, with the average annual rainfall of 900 mm. The average annual temperature is 12 °C, with 220 frostless days. It also has four distinct seasons under the influence of the ocean monsoon.

The study area is located in the Dagu river and Yanghe river estuary. As the mother river of Qingdao, the drainage area of Dagu river is 6131.3 km², accounting for about 85.6% of total flow of four major river, such as Dagu river, Moshui river, Baisha river and Yanghe river, that eventually enters into the Jiaozhou Bay. The Dagu river wetland is the largest wetland in Qingdao. The main stream length of Yanghe river is about 49 km, with the drainage area of 303 km². Yanghe river wetland grew a wide range of spartina, which was brought in from foreign countries in 1963. It had become an important sample site of spartina.

2.2. Sampling methods

Samples were collected from four representative types of wetlands in the Jiaozhou bay including the naked tidal (GT), suaeda salsa wetland (JP), reed wetland (LW), and spartina wetland (DMC) in winter (January), spring (April), summer (July), Autumn (October) of 2014. As shown in Fig. 1, the GT, JP, and LW distributed along Dagu river from sea to land. The DMC was a typical invasive species in Jiaozhou Bay, distributing in the Yanghe estuary.

According to the hydrological conditions and vegetation distribution, a different number of sampling points (two in LW, three in JP, four in GT, and two in DMC) were set in each wetland. Three parallel soil profiles were sampled in each sampling region.

The samples were obtained from those soil profiles at the height of 0–10, 10–20, 20–40 and 40–60 cm. The soil examples taken with cutting ring were used to measure the bulk density. All soil samples were placed in zip-lock bag immediately, and transported to the laboratory. After drying at room temperature, the visible plant and animal residues were removed from soil samples. Additionally, all soil samples were sieved through a 100 mesh sieve, and then stored for the next measure.

2.3. Analytical methods

The content and structure of DOM in soil was determined using colorimetric assay (Zhan and Zhou, 2002). Briefly, about 10 g

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