# The chemical composition and source identification of soil dissolved organic matter in riparian buffer zones from Chongming Island, China

Yulai Wang, Changming Yang*, Jianhua Li, Shuo Shen

*Key Laboratory of Yangtze River Water Environment of the Ministry of Education, Tongji University, Shanghai 200092, China*

## HIGHLIGHTS

- Chemical fractions of DOM varied with riparian vegetations and human activities.
- The hydrophobic and amphiphilic fractions are dominant in the riparian soil DOM.
- DOM were derived from riparian plants, domestic sewage and agricultural activities.
- LC-Q-TOF-MS can be applied to characterize DOM chemical composition and sources.

## ARTICLE INFO

## ABSTRACT

Dissolved organic matter (DOM) that is derived from the soil of riparian buffer zones has a complex chemical composition, and it plays an important role in the transport and transformation of pollutants. To identify the source of DOM and to better understand its chemical and structural properties, we collected 33 soil samples from zones with fluctuating water levels along the major rivers on Chongming Island, evaluated the DOM contents in riparian soil, analyzed the chemical composition and functional groups and traced DOM origins by using liquid chromatography quadrupole time-of-flight mass spectrometry (LC-Q-TOF-MS) combined with clustering analysis. All sampling sites were divided into four groups by principal component analysis (PCA) on the basis of the DOM molecules. The results showed that there was no significant difference in the DOM contents between every two groups; however, the DOM fractions differed significantly among the different site groups in the following order: $\Sigma$ lipids and $\Sigma$ proteins > $\Sigma$ sugars and $\Sigma$ fatty acids > $\Sigma$ amino acids, $\Sigma$ indoles and $\Sigma$ alkaloids. DOM in the riparian buffer zones originated from riparian plants, domestic sewage and agricultural activities, and the hydrophobic and amphiphilic fractions accounting for over 60% of the identified molecules were the dominant fractions. Our study has confirmed the heterogeneous properties of DOM, and it is of vital importance to isolate and characterize the various DOM fractions at the molecular level for a better understanding of the behavior and roles of DOM in the natural environment.

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## 1. Introduction

Dissolved organic matter (DOM) is widely distributed in natural ecosystems, including natural water bodies, the atmosphere and soils and sediments. DOM is a complex mixture of aromatic and aliphatic hydrocarbon structures, and it contains diverse functional groups such as amides, carboxyls, hydroxyls, ketones and other minor groups (Leenheer and Croué, 2003; Pernet-Coudrier et al., 2011). Moreover, DOM plays significant roles in ecosystem functions, influencing the global carbon and nitrogen cycles through movements of dissolved organic carbon (DOC) and dissolved organic nitrogen (Opsahl and Benner, 1997; Inamdar et al., 2012), altering the optical properties and aesthetic appearance of natural water bodies (Schindler et al., 1997; Leenheer and Croué, 2003) and consequently resulting in changes to the physical and chemical behavior and bioavailability of natural and discharged compounds (Hassett, 2006). Therefore, the presence of DOM in natural ecosystems can pose risks for aquatic organisms and even results in risks to human health through the food chain. For these reasons, extensive studies have been performed on DOM over the past few decades.

* Corresponding author. Address: College of Environmental Science and Engineering, Tongji University, 1239 Siping Road, Shanghai 200092, China. Tel.: +86 21 55962975; fax: +86 21 65986313.

*E-mail addresses:* tjwangyulai@gmail.com (Y. Wang), cmyang@tongji.edu.cn (C. Yang), leejianhua@tongji.edu.cn (J. Li), shenshuo1989@126.com (S. Shen).

DOM harbors both hydrophilic and hydrophobic groups at the molecular level, and hydrophilic fractions include carbohydrates, carboxylic acids and protein/peptides; the hydrophobic fraction is composed of humic, aromatic and polyphenol components (Qualls and Haines, 1991). These micelle-like DOM properties cause it to bind with other hydrophobic molecules by hydrogen bonds, electron transfer, van der Waals forces and ion exchange, and this binding decreases a hydrophobic molecule's apparent volatility, bioavailability and apparent solubility (Hassett, 2006). DOM was well known as a fundamental and important molecule in many biogeochemical processes in soil and natural water systems. Therefore, it is important to study DOM composition to understand the role of this material in biogeochemical cycling and its transport into aquatic systems.

Riparian buffer zones play an important role in transferring DOM between terrestrial and aquatic ecosystems and also affect fluvial DOM cycling. At present, the ecological and environmental function of the riparian zone has been well reported, and most studies have focused on nitrification and denitrification as agricultural non-point source pollution (Mankin et al., 2007; Ivits et al., 2009). Recent reports on DOC in riparian soil (Samaritani et al., 2011; Batlle-Aguilar et al., 2012) have focused on DOC quantity. However, there are few reports concerning the chemical composition and functionality of DOM in the riparian buffer zone (Kalbitz et al., 2000, 2003; Marschner and Kalbitz, 2003). The primary causes for this situation are limitations in the available analytical methods.

Recent breakthroughs in instrument design have presented liquid chromatography quadrupole time-of-flight mass spectrometry (LC-Q-TOF-MS) as a possible solution to this conundrum in which it is too complex to detect the exact chemical compositions of complex mixtures. Because of its unambiguous identification, high sensitivity and fair reproducibility in quantitatively identifying complex compounds, LC-Q-TOF-MS has been used to probe the chemical compositions of pesticides (Ferrer and Thurman, 2007), pollutants (Masiá et al., 2012) and their metabolites (Ciborowski et al., 2010). Our objectives were to gain insights into the chemical compositions and functional groups of DOM extracted from riparian soil and to probe the impact of riparian vegetation and agricultural activities on DOM composition. We examined DOM quantities (DOC contents) in riparian soil and analyzed the origins, chemical compositions and functional groups in DOM that was extracted from the riparian soil of Chongming Island, China. Specific attention was paid to the DOM source in different riparian buffer zones. The present results can improve our understanding of the source and transformation of DOM in a plains watershed.

## 2. Materials and methods

### 2.1. Sampling site descriptions and soil sampling

As the third largest island in China and the largest alluvial island in the world, Chongming Island (31°25′–31°38′N and 121°50′–122°05′E) is located in the Yangtze River estuary of eastern China, and it covers 1041 square kilometers. This island is representative of plains watersheds, and the water surface area reaches up to 9% of Chongming Island. Many channels were excavated from the 1950s–1960s to obtain fresh water in northern Chongming Island and to control floods. The flora, biodiversity, structure and functions of riparian buffer zones in these channels have been well-developed over the past 60 years, which has facilitated the fluvial functions of these channels. Chongming Island has a northern sub-tropical monsoon climate with an average annual temperature of 15.3 °C, and the average April temperature

is 13.7 °C. The average annual precipitation is 1022 mm, with 60% of rainfall occurring between May and September. The average humidity is approximately 82% (Huang et al., 2008).

Because of frequent alternately moist and dry conditions, the zones with fluctuating water levels have a substantial impact on the fate and transport of DOM to receiving water. To understand the influences of riparian vegetation and agricultural activities on the DOM composition, soil samples were collected from zones with fluctuating water levels in natural or semi-natural riparian zones of Chongming Island (Fig. 1). Three replicates of surface soil samples (0–15 cm) were collected from 1 m × 3 m sampling scopes in April of 2011. One soil profile, which was composed of three replicates, was collected at site J3 and sliced at 10-cm intervals from the top down to the bottom (60 cm). Stones and woody debris were removed from the collected soils, which were mixed thoroughly onsite to obtain a representative soil sample and preserved in sterilized bags at 4 °C until use. All soil samples were air-dried, gently ground with a roller and passed through 2 mm sieve for analysis of soil physiochemical parameters and 0.107 mm sieve for soil DOM extraction, respectively.

To provide a clear overview of soil sampling sites with correlated groups, we divided all 33 sampling sites into four groups based on the distribution of DOM chemical compositions by principal component analysis (PCA). The first group (Group A) included seven soil samples from the Bayao and Tuanwang rivers, which are located in eastern Chongming Island. Organic agriculture rather than traditional agriculture is a major production system in this region where few commercial fertilizers and pesticides were used; Group B included four soil samples, all of which were collected from Beiheng River, which passed through northern Chongming Island. There was intensive agriculture and livestock breeding plants in Group B, which resulted in a large amount of nonpoint-source pollution and wastewater rushing into the adjacent buffer zones. Group C yielded seven soil samples including C4 and the six soil profile slices from the Cangfang and Jie rivers. The primary land use in Group C district was distributed agriculture, and even some riparian zones were cultivated with some crops. The last group (Group D) included 15 samples that were collected from the Miao, Gelong, Dongping, Zhi and Xinjian rivers, which are located in western and central Chongming Island. Nearly 50% of the population inhabited Group D, and a large amount of raw domestic wastewater ran into riparian buffer zones because of a lack of sewage treatment plants on Chongming Island.

### 2.2. Soil sample preparation and analysis

The DOM was extracted according to the Ohno method (Ohno and Bro, 2006). Five g of soil sample (sieved at 0.107 mm) was extracted with 50 mL of deionized distilled water (DI-$H_2O$) by shaking for 24 h at 20 °C in the dark, and the suspensions were centrifuged at 3000 rap $min^{-1}$ at 4 °C for 20 min and filtered through 0.45 µm GF/F filters (Whatman). The extraction was analyzed for DOC content by high temperature combustion method on a TOC-V$_{CPH}$ (Shimadzu). Three to five replicates were performed for each sample, resulting in a typical coefficient of variation < 2%.

The soil bulk density was determined with undisturbed oven-dried cores as the mass per volume of oven-dried soil (Anderson et al., 1988). The moisture and electrolytic conductivity (EC) were determined by WET Sensor (WET-2, England) (Mishra and Salokhe, 2008), and the soil salinity and pH (soil water extract) were measured by using an HACH apparatus (HQ40, USA) according to a modified Wakushima method (Wakushima et al., 1994). The soil of the tested sample is a calcareous alluvial type with a sandy texture. The pH of the tested soils ranged from 7.34 to 8.91 (1:5 w/w soil/water), the moisture contents ranged from 46.02% to 52.78%,