Marine Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Dissolved organic matter in coastal rainwater: Concentration, bioavailability and depositional flux to seawater in southeastern China

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ARTICLE INFO

Keywords:
Rainwater
Dissolved organic carbon
Bioavailability
Fluorescence EEM

ABSTRACT

Forty-seven precipitation samples were collected between March 2011 and May 2012 in Xiamen, southeastern China to examine the concentration, bioavailability and depositional flux of dissolved organic matter (DOM) in rainwater. Fluorescence excitation-emission (EEM) spectra of DOM were also determined to trace compositional changes during biodegradation experiments to assess which components of the DOM pool are biolabile. Rainwater dissolved organic carbon (DOC) concentrations ranged from 8.5 to 932 μM, with a volume-weighted average concentration of 128 μM. The fraction of biolabile DOC (BDOC%) ranged from 16 to 91% with an average of 46 ± 17%. The biodegradation rate of rainwater DOC followed a first-order exponential curve. During biodegradation experiments, protein-like fluorescence decreased and humic-like fluorescence remained constant or increased. Both DOC and BDOC concentration showed a dilution effect in relation to rainfall amount. Rainwater with continental trajectories typically had higher DOC concentrations than from marine trajectories, while, in contrast, the BDOC% didn't show significant differences among trajectories. Winter rainwater DOC concentration was significantly higher, while BDOC% was lower than other seasons, which may be related to greater relative fossil fuel inputs, particularly from coal burning in northern China. The depositional flux of rainwater DOC into Xiamen Bay was estimated to be 2.1 Gg C yr^{-1}, and the rainwater BDOC flux to Xiamen Bay was approximately 35% of that discharged from the Jiulong River. Our results highlight that precipitation inputs play a significant role in supplying BDOC to the ocean with ramifications for marine food webs.

1. Introduction

Rainwater annually deposits approximately 90 Tg of dissolved organic carbon (DOC) to the global ocean (Willey et al., 2000), representing an important carbon source to marine ecosystems (Iavorivska et al., 2017; Willey et al., 2000). Bioavailable DOC (BDOC) is the fraction of organic carbon that can be readily utilized by microorganisms and allochthonous sources (e.g. precipitation, groundwater, rivers) of BDOC to the ocean are a crucial component in the global carbon cycle as they can fuel oceanic secondary productivity and affect food webs (Azam et al., 1983; Avery et al., 2003). The results of limited studies to date have indicated a much higher bioavailability of rainwater DOC (> 50%) than riverine DOC (1–30%) (Avery et al., 2003; del Giorgio and Davis, 2003; Fellman et al., 2014; Fellman et al., 2009; Guo et al., 2014; Gan et al., 2016; Godoy-Silva et al., 2017; Spencer et al., 2015; Yang et al., 2013a). This is highlighted by a recent study in the southeastern United States which demonstrated that rainwater deposited more BDOC to the coastal ecosystem than derived from riverine discharge (Avery et al., 2003). Considering the amount of rainwater DOC input to the ocean and its high bioavailability, the rainwater input of BDOC may be significant even at the global ocean scale but to-date it remains poorly quantified.

Rainwater dissolved organic matter (DOM) collected over inland and near-coastal regions comprises a complex mixture of multiple sources, including biomass and fossil fuel burning, secondary organic aerosols (SOAs), dust and ocean spray (Bao et al., 2017; Mead et al., 2013). The concentration and composition of rainwater DOM is highly temporally and spatially variable (Iavorivska et al., 2016; Kieber et al., 2006; Mitra et al., 2013; Willey et al., 2000; Wozniak et al., 2014). Previous studies have shown that air mass sources, rainfall amount and anthropogenic activities (e.g., biomass and fossil fuel burning) can all affect rainwater DOC concentrations (Avery et al., 2006; Coelho et al., 2008; Godoy-Silva et al., 2017; Kieber et al., 2002; Li et al., 2016; Pantelaki et al., 2018; Yan and Kim, 2012). However, it remains

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https://doi.org/10.1016/j.marchem.2018.07.008
Received 4 May 2018; Received in revised form 11 July 2018; Accepted 20 July 2018

unknown how these factors would affect the bioavailability of rainwater DOM. This is important, as if the temporal and spatial variation of rainwater BDOC is significant, then it will naturally have different ecological impacts on receiving marine environments.

Fluorescence excitation-emission (EEM) spectra of DOM have been shown to be a useful and efficient analytical technique for the examination of chromophoric DOM (CDOM) in natural waters (Coble, 2007), including characterizing the composition, source, and processing of rainwater DOM (Miller et al., 2009; Mitra et al., 2013, 2017; Salve et al., 2012; Zhang et al., 2014). For instance, by analyzing EEM fluorescence spectra, Mitra et al. (2017) reported terrestrial SOAs and fossil fuel derived aromatics in rainwater DOM. The various fluorescent components can then be applied to track the changes of fluorescent DOM (FDOM) during mixing, biological degradation, and photo processing in natural waters (Guo et al., 2014; Helms et al., 2013; Kieber et al., 2012; Tanaka et al., 2014; Wang et al., 2017), and thus may provide a useful tool in tracing the compositional changes in rainwater DOM during microbial degradation.

Affected by monsoons and typhoons, southeastern China has high annual precipitation ($> 1200\ mm\ yr^{-1}$) (Wang and Zhou, 2005). This region is influenced by air masses from both land and ocean trajectories. During winter, northern China is heavily affected by biomass and fossil fuel burning, under the influence of northeast winds, those air masses are exported to southeastern China. While during summer, under the influence of southwest winds and typhoons, air masses are predominantly derived from the ocean. Therefore, southeastern China provides an interesting region for studying how different air masses (especially terrestrial vs. maritime) and associated pollutant loads will affect rainwater DOC and BDOC. Here we present a seasonal rainwater DOC and bioavailability study from a coastal city (Xiamen) in southeastern China. The objectives of this study are: 1) to characterize the seasonal variability of rainwater DOC concentration; 2) to estimate the bioavailability of rainwater DOC and how different DOM components were altered during microbial degradation; 3) to examine how different factors such as rainfall amount and air mass trajectories impact rainwater DOC concentration and bioavailability; and 4) to estimate the flux of rainwater DOC to the receiving ecosystem and evaluate its significance.

2. Materials and methods

2.1. Study site and sample collection

Xiamen, next to the Taiwan Strait, is a typical coastal city located in southeastern China. The region has a subtropical oceanic monsoon climate with northeast winds that prevail from October to March, and southeast winds from April to September. As the site is affected by the monsoon and typhoons, the average annual rainfall is 1350 mm, of which ~70% occurs between April and September (http://en.weather.com.cn/). Xiamen Bay is the receiving coastal area and encompasses approximately 1000 km^2.

Forty-seven rainwater samples (#1 - #47) were collected at Site 1 (24.43°N, 118.09°E; Fig. 1), which is located in an open area (i.e. no vegetation or building inputs) of the main campus of Xiamen University and is about 50 m away from Xiamen Bay from March 2011 to May 2012. Detailed sampling times can be found in Supplementary Table S1. To assess rainwater DOM biodegradation rates and compositional changes, two additional rainwater samples (#48 and #49) were collected at Site 2 (24.60°N, 118.32°E), located at the Xiang'an campus of Xiamen University from February 18th, 2014 from 19:00 to February 19th, 2014 at 19:00 and on February 26th, 2014 from 9:00 to 19:00, respectively. Site 2 is ~1 km away from Xiamen Bay and ~28 km away from Site 1.

All rainwater samples were collected using pre-cleaned and pre-combusted glass beakers placed 20 m above the ground and > 70 cm higher than the floor to avoid contamination by droplet splashes. All

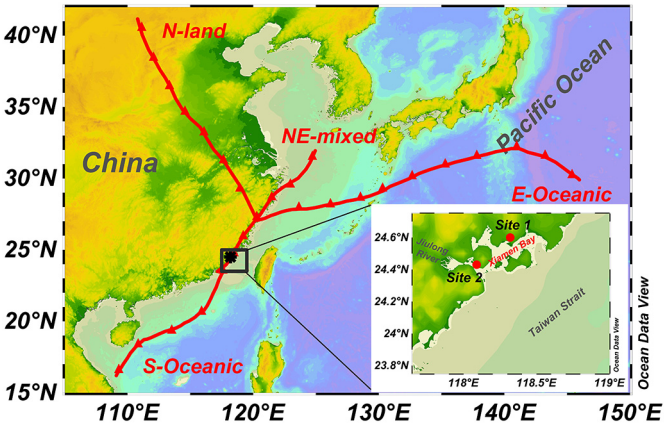

Fig. 1. Rainwater sampling sites and typical air mass trajectories. Red dots denote the sampling locations and red lines denote the air mass trajectories. N-land: strictly terrestrial back-trajectory from the north; *E*-oceanic and S-oceanic: marine back-trajectories from the east and south, respectively; NE-mixed: mixed trajectory from the northeast of China (Strayer et al., 2007). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

glassware used for DOC collection, including collection beakers and storage containers, were soaked with HCl (1 M) for at least 24 h, and rinsed with Milli-Q water (18.2 MΩ) at least three times and subsequently combusted at 550 °C in a muffle furnace for 5 h to remove organics prior to use. Beakers were replaced with a dry muffled beaker after each event. After collection, samples were immediately filtered through a GF/F filter (pre-combusted at 450 °C for 5 h), and then acidified to pH = 2 by HCl (GR) and stored at −20 °C until DOC analysis. Previous studies have shown that the majority of organic carbon in rainwater is in the dissolved form (Jurado et al., 2008; Kanakidou et al., 2012; Likens et al., 1983; Willey et al., 2000), therefore, to avoid possible contamination, rainwater samples were not filtered for the BDOC experiments. A comparison of BDOC% of two samples (#48 and #49) was undertaken between the filtered and unfiltered samples in our study and confirmed that BDOC% was similar between the two treatments (refer to Supplementary Fig. S1).

Meteorological data including rain amounts during the sampling period and storm origin were recorded from https://rp5.ru/. Detailed rainfall information is provided in Supplementary Table S1.

2.2. Microbial incubation experiments

Two separate microbial incubation experiments were designed to assess different objectives.

2.2.1. Rainwater bioavailable DOC (BDOC)

Microbial incubation experiments were conducted using methods similar to those used in past studies (Aminot et al., 1990; Avery et al., 2003; Fukushima et al., 2001; Hung et al., 2003; Lønborg et al., 2010; Yang et al., 2015). Briefly, rainwater samples (~60 mL) in triplicate (collected in a beaker and separated into three glass bottles) with native microbial community were placed in the dark immediately after sampling and incubated at room temperature (~25 °C) for 28 days to determine the BDOC% of samples collected from March 2011 to June 2012. Due to limited volume of rainwater, samples #10, #11, #23, #24, #30 and #32 were not incubated.

BDOC% was considered as the percentage of DOC loss during the incubation experiment:

$$BDOC\% = (DOC_{0d} - DOC_{28d})/DOC_{0d} \times 100\%. \quad (1)$$

where DOC_{0d} is the DOC concentration at 0d and DOC_{28d} is the final DOC concentration at 28d.