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

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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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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 ($> 1200 \, \mathrm{mm \, yr^{-1}}$) (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 km².

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
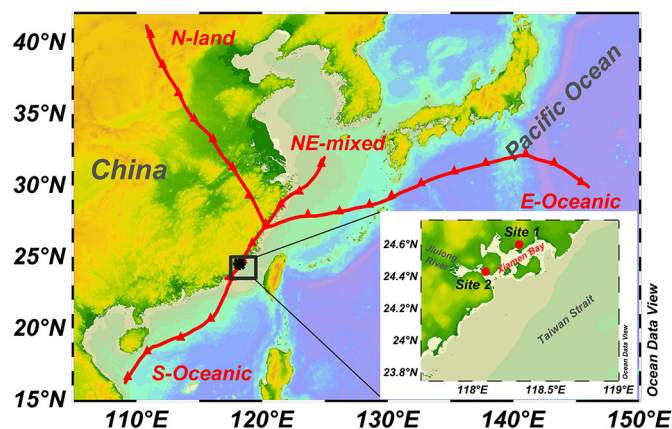

Fig. 1. Rainwater sampling sites and typical air mass trajectories. Red dots denote the sampling locations and red lines denote the air mass trajectories. N-land: strictly terrestrial back-trajectory from the north; E-oceanic and S-oceanic: marine back-trajectories from the east and south, respectively; 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:

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

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

2.2.2. Degradation rate

To examine the degradation rate of rainwater DOC and the changes in DOM fluorescence components, two rainwater samples (#48, #49) collected at Site 2 in February 2014 (Fig. 1) were incubated using the same method, under the same conditions (dark at room temperature) as the rainwater BDOC experiment. Subsamples were collected at 0d, 1d, 3d, 6d, 10d, 16d (due to limited volume of rainwater, there was no sample for #49 for this time point), and 28d, respectively. At all time points, DOC concentration and FDOM was measured on the triplicates.

2.3. DOC and FDOM measurements

DOC concentration was determined with a Multi N/C 3100 TOC-TN analyzer (Analytik Jena, Germany) (Guo et al., 2011). Acidified samples were purged with oxygen for 8 min to remove the inorganic carbon before high temperature catalytic oxidation. Potassium hydrogen phthalate was used as a standard for DOC calibration. All measurements were performed in triplicate with a fixed instrumental variance < 2%. Low carbon water (1–2 μM) and deep seawater reference samples (44–46 μM) from the Sargasso Sea provided by Dr. Hansell's laboratory at the University of Miami were used for quality control. The standard deviation of the replicate measurements of the deep Sargasso Seawater was ± 1.9 μM.

EEM fluorescence spectra were obtained using a Cary Eclipse (Varian, Australia) fluorometer equipped with a 150 W Xe arc lamp. The emission spectra were scanned every 2 nm at wavelengths from 250–600 nm, with excitation wavelengths of 250–450 nm at 5 nm intervals. The EEMs of samples were Raman calibrated and subtracted from a Raman normalized Milli-Q water EEM scanned on the same day (Murphy et al., 2010). The EEM spectra were modeled by PARAFAC, using MATLAB 7.1 with the DOMFluor toolbox (Stedmon and Bro, 2008). Split-half validation was used to determine the number of fluorescent components. The fluorescence intensity of each fluorescent component was evaluated by the maximum fluorescence, Fmax (RU, i.e., Raman units) (Kowalczuk et al., 2009; Stedmon et al., 2003; Stedmon and Markager, 2005).

2.4. Back-trajectory analysis

Single back-trajectory analysis was run for each precipitation event starting at the recorded onset of precipitation utilizing National Oceanic and Atmospheric Administration (NOAA): *HTTP://ready.arl.noaa.gov/HYSPLIT.php.*. Trajectories were generated for a 72 h hind-cast. Trajectories were run starting at the 500 m level to represent the air mass near the well-mixed boundary layer likely to contribute more heavily to in-cloud processes and wet deposition. All rain events were visually categorized based on origin (compass direction) and pathway into the following four categories: 1) strictly terrestrial back-trajectory from the north (N-land); 2 and 3) marine back-trajectories from the east and south (*E*-oceanic and *S*-oceanic, respectively); and 4) mixed trajectory from the northeast of China (NE-mixed) (Strayer et al., 2007) (Fig. 1).

2.5. Calculation of the volume weighted average (VWA) DOC and VWA BDOC

The VWA DOC was calculated using the following equation:

$$\text{VWA DOC} = \frac{\sum_{i=1}^{i=47} (C_i \times V_i)}{\sum_{i=1}^{i=47} V_i} \tag{2}$$

Where i represents sample number, C_i represents the DOC concentration of ith sample, and V_i represents the sampling volume of ith sample. VWA BDOC was calculated using the same method.

2.6. Depositional flux of rainwater DOC and BDOC to Xiamen Bay

Rainwater DOC flux to Xiamen Bay was estimated following the equation outlined by Avery et al. (2003):

$$F = C \times H \times S \tag{3}$$

where F represents the flux, and C, H and S represents the VWA DOC, annual rainfall amount and the receiving area, respectively. The average annual rainfall in Xiamen is 1350 mm, and the area of Xiamen Bay is roughly 1000 km². The same equation was used to estimate the flux of bioavailable DOC to Xiamen Bay factoring in the proportion of bioavailable DOC.

2.7. Statistical analysis

Pearson's correlation was used to test the relationship between DOC and BDOC concentration. A *t*-test was performed to analyze the difference of BDOC% among different seasons and air masses. All the analyses were performed using SPSS 13.0 for Windows (SPSS Inc., USA).

3. Results

3.1. Concentration of rainwater DOC

DOC concentration ranged from 8.5 μM to 932 μM (Fig. 2a), with a volume-weighted average DOC (VWA DOC) value of 128 μM. The majority of samples had DOC concentrations < 400 μM (Fig. 2a). Seasonal variability was apparent in the samples with the highest VWA DOC concentration occurring in winter (197 μM), followed by spring (152 μM) and summer (123 μM), and the lowest observed in autumn (88 μM) (Fig. 2a). Highest VWA DOC values were observed in rain events sourced as N-land (184 μM), followed by N*E*-mixed (176 μM), S-oceanic (145 μM) and E-oceanic (64 μM) (Fig. 3). A significant inverse relationship (p < 0.05) was found between DOC concentration and rainfall amount (Fig. 4).

3.2. Biodegradation of rainwater DOC

BDOC concentration ranged from 5.4 μM to 307 μM (Figs. 2b and 4), with a volume-weighted average BDOC of 61 μM. The BDOC concentration is also highly significantly correlated with the initial DOC concentration ($r = 0.93$, n = 41, p < 0.01) (Fig. 5). The BDOC% ranged from 16% to 91%, with an average value of 46 ± 17% (mean ± 1 s. d.) (Fig. 2b). The BDOC% was significantly lower in winter (33%) than other seasons (spring: 49%, summer: 52% and autumn: 52%) (Fig. 2b; *t*-test, all p < 0.05). The BDOC% for the four types of back trajectories were all on average higher than 40%, and were not significantly different from one another (t-test, p > 0.05) (Fig. 3). Similar to DOC concentration, BDOC concentration (not BDOC%) also showed a significant inverse correlation with rainfall amount (Fig. 4), while the BDOC% did not correlate to rainfall amount (p > 0.05, figure not shown).

The microbial incubation experiments examining degradation rates (#48 and #49 collected at Site 2) exhibited BDOC values of 69% and 55%, respectively, which was within the range of samples collected at Site 1. Both samples #48 and #49 showed an exponential decreasing trend with incubation time (Fig. 6a), suggesting a first order decay of rainwater DOC, The degradation rate constant was calculated following the equation suggested by Lønborg et al. (2010):

$$\text{DOC}(t) = \text{BDOC}^* \exp(-k\text{DOC}^*t) + \text{RDOC} \tag{4}$$

where DOC(t) is the concentration of DOC at time t, BDOC the bioavailable pool (μM), kDOC the degradation rate constant (d^{-1}), t the time (days) and RDOC the residual pool at the end of the incubations (μM). The degradation rate of #48 and #49 were 0.15 d^{-1} and 0.051
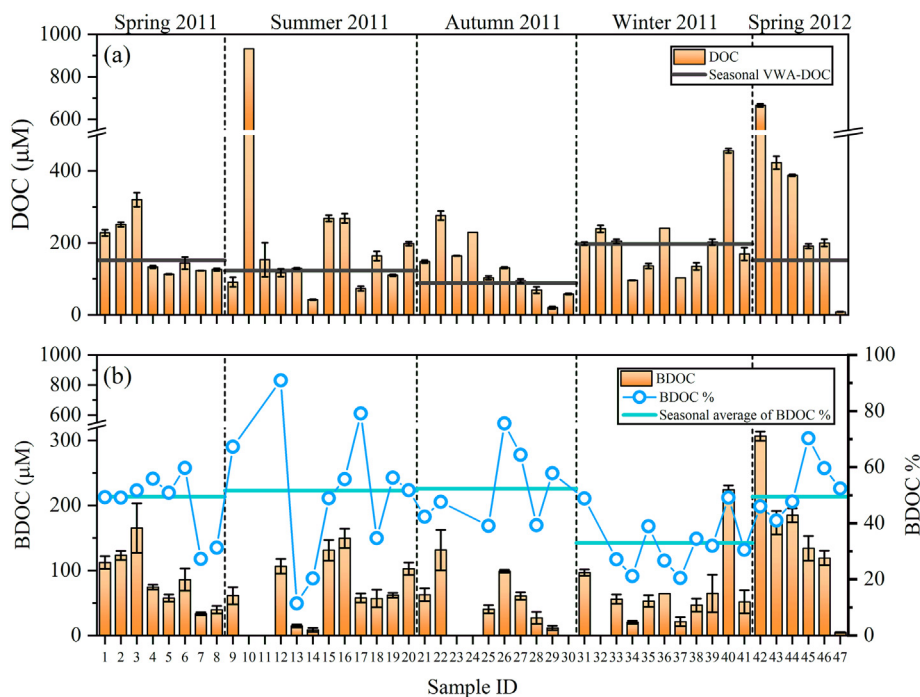
Fig. 2. DOC concentration (a) and BDOC and the proportion of BDOC (BDOC%) (b) in rainwater samples. Lines in (a) and (b) represents seasonal VWA-DOC and the average of BDOC%, respectively. Error bars in (a) represent standard deviation and in (b) represent the propagated errors considering the standard deviation of initial and final DOC concentration during incubation experiments.
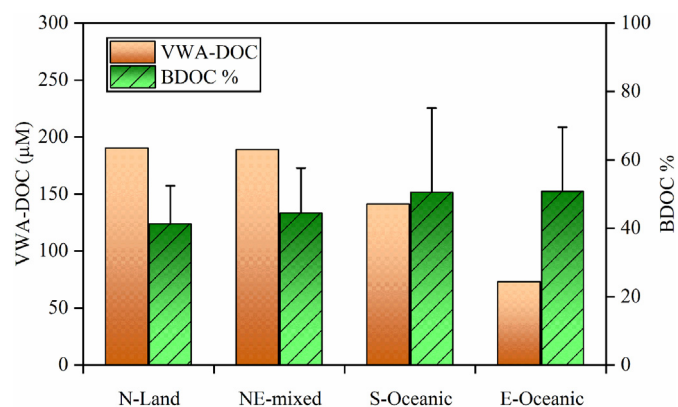

Fig. 3. VWA-DOC concentration and BDOC% in varied trajectory rain events. Error bars represent standard deviation.
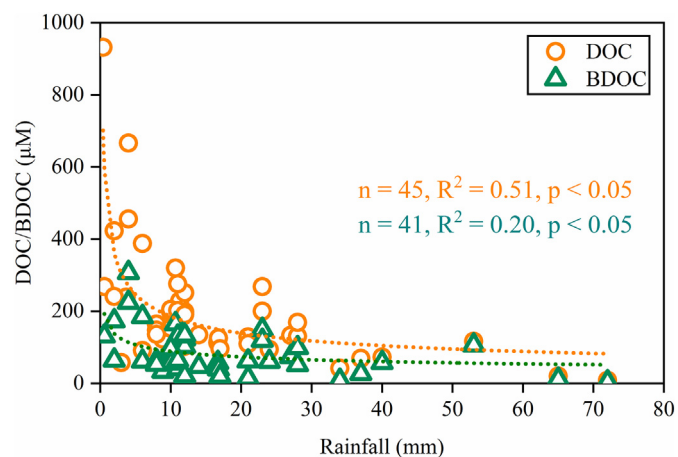

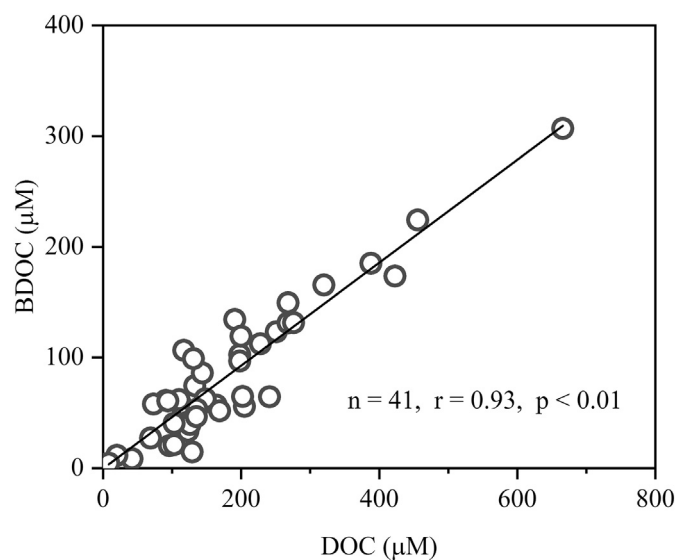**Fig. 4.** Relationship between rainwater DOC or BDOC and rainfall amount during sampling period.

Fig. 5. The relationship between BDOC concentration and DOC concentration.

d^{-1}, respectively (Fig. 6a).

3.3. Fluorescent components in rainwater DOM during microbial degradation

Four fluorescent components (C1, C2, C3 and C4) were identified using EEMs-PARAFAC (Supplementary Fig. 2). C1 (< 250 (325)/436), C2 (< 250, 310/388 nm) and C3 (250, 350/450 nm) are humic-like components. C1 and C3 contain components that were traditionally defined as peak A and peak C and were considered to be of terrestrial origin, or produced by microbial degradation (Coble et al., 1998). C2 (< 250, 310/388 nm) contained marine humic-like peak A and peak M (Coble et al., 1998). C4 (270/304, 370 nm) is a protein-like component. During the microbial degradation experiments protein-like fluorescence decreased and humic-like fluorescence remained constant or increased with time (Fig. 6b, c).
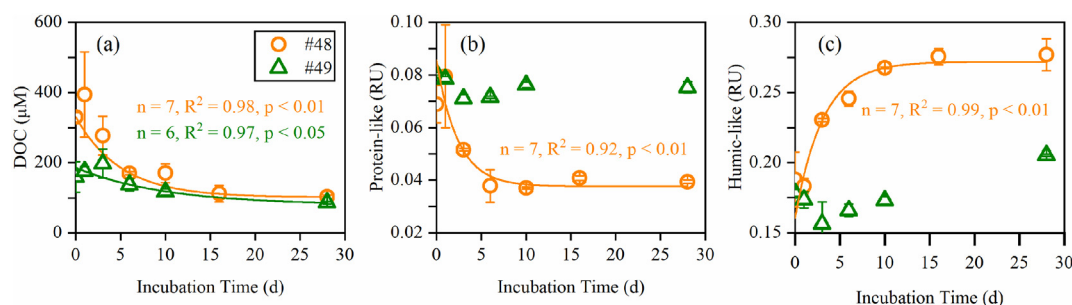
Fig. 6. Degradation of rainwater DOC (a) and fluorescent components (b, c) in the intensive time series incubations for samples #48 and #49.

3.4. Depositional flux of rainwater DOC and BDOC to Xiamen Bay

The annual rainwater DOC flux is estimated as 2.1 g C m^{-2} yr^{-1} and a total amount of 2.1 Gg C yr^{-1} to Xiamen Bay. The depositional flux of rainwater bioavailable DOC to Xiamen Bay was estimated as 1.0 Gg C yr^{-1}.

4. Discussion

4.1. Rainwater DOC concentration and influencing factors

The rainwater DOC concentration in Xiamen (8.5 to 932 μM) was within the range reported for other coastal regions (Avery et al., 2006; Avery et al., 2003; Kieber et al., 2006; Lara, 2001; Willey et al., 2000), and the VMA-DOC (128 μM) was close to the median value collected from 22 coastal sites around the world (Iavorivska et al., 2016). The more than two order of magnitude variation in one location exhibited in our study suggests that rainwater DOC concentration is highly variable.

Numerous factors could influence rainwater DOC concentration, such as rain amount (Kieber et al., 2006; Li et al., 2016; Santos et al., 2013; Zhang et al., 2014), local emissions (Coelho et al., 2008) and air mass sources (Kieber et al., 2002). The highest DOC concentration observed in this study was in sample #10, collected in summer, following a period of approximately 20 days without rain. During this dry period a large amount of aerosols accumulated in the atmosphere (organic carbon concentration in PM 2.5 was much higher in the sampling day than days nearby, personal communication with Prof. Xinhong Wang). The rain event was also extremely small (only a 20 mL sample was collected) and therefore a large amount of organic carbon was flushed out by a small amount of water, resulting in the subsequent high DOC concentration (932 μM). The lowest DOC concentration was observed in sample #47 (9.5 μM), which conversely was collected during an extreme rain event, where DOC was diluted by the large amount of rainwater. A dilution effect is apparent when all the samples were considered (Fig. 4).The significant inverse correlation between DOC and rainfall amount indicates the rapid wash out of atmospheric sourced DOC. The dilution effect for rainwater DOC concentration has also been observed in other regions (Kieber et al., 2006; Li et al., 2016; Santos et al., 2013; Zhang et al., 2014). DOC in rainwater mainly contains organic acids, proteins and amino acids, formaldehyde, acetaldehyde, and "humic" components (Kieber et al., 2006; Tang, 1998), and this broad array of organic materials show diverse water solubility and subsequently varied scavenging characteristics during rain events. Interestingly, in all these studies, the dilution effect became less significant when rainfall amount was higher than approximately 10 mm, suggesting that washing out of rainwater DOC was achieved at moderate rainfall amounts.

Storm origins and trajectories have also been shown to impact rain DOC concentration (Kieber et al., 2006; Kieber et al., 2002; Muller et al., 2008). The higher VWA DOC in terrestrially influenced rain events (Fig. 3) than maritime events is consistent with previous studies

(Kieber et al., 2006, Kieber et al., 2002; Muller et al., 2008). Both S-oceanic and E-oceanic air masses originated predominantly from the marine environment, however, the DOC concentrations varied greatly. This is because the E-oceanic rain events in Xiamen have almost no land influence as they originate from the Pacific Ocean, while the S-oceanic rain may entrain terrestrially and anthropogenically sourced materials over Southeast Asia. In addition to the influence of air mass origin, seasonal variation is also apparent (Fig. 2). In winter, the predominant northeast winds bring a large amount of anthropogenically sourced material from north China, including organic matter from the increased burning of biomass and fossil fuel materials, especially coal (Feng et al., 2006; Shen et al., 2009; Zhang et al., 2011a), resulting in higher DOC concentrations. An earlier study also noted higher OC in aerosols in Xiamen during winter and attributed this to long-distance transport from north China (Zhang et al., 2011b).

4.2. The bioavailability of rainwater DOC and its influencing factors

The average Xiamen rainwater BDOC% was slightly lower than values previous reported from the North Carolina coast and São Paulo state (Avery et al., 2003; Godoy-Silva et al., 2017). Nonetheless, all studies showed much higher BDOC% in rainwater than typical values for river water BDOC% (typically < 30%) (Avery et al., 2003; del Giorgio and Davis, 2003; Fellman et al., 2014; Fellman et al., 2009; Gan et al., 2016; Spencer et al., 2015; Yang et al., 2013a). Similar high BDOC% was observed in glacier ice and glacier streams, which was partly attributed to the contribution of organic material via atmospheric deposition (Stubbins et al., 2012; Spencer et al., 2014). Recent studies also demonstrate that the fraction of biostable DOM (represented by dissolved black carbon) is much smaller in the water soluble fraction of marine aerosols in comparison to riverine waters (Bao et al., 2017; Jaffé et al., 2013), further implying the potentially greater bioavailable nature of DOM in rainwater.

Even though rainwater BDOC% is poorly studied to-date, the composition of rainwater DOM has been characterized by a number of different techniques and in various locations in the past decade (Altieri et al., 2009; Cottrell et al., 2013; Kieber et al., 2006; Mead et al., 2013; Miller et al., 2009; Mitra et al., 2017; Muller et al., 2008; Santos et al., 2009; Seaton et al., 2013), which enables us to infer the potential reason for the high rainwater BDOC%. By using ultrahigh resolution mass spectrometry and molecular marker measurements, organic acids (e.g., formic, acetic, lactic etc.), carbohydrates and proteins have been found in, and sometimes are important contributors to rainwater DOC or the water soluble fraction of aerosols (Altieri et al., 2009; Kieber et al., 2002; Mead et al., 2013; Tang, 1998; Wozniak et al., 2014; Wozniak et al., 2008). These fractions of organic matter are viewed as readily biologically available (Willey et al., 2000). Additionally, fluorescence EEMs have shown the extensive presence of protein-like fluorescent DOM in rainwater (Santos et al., 2009). In this study the degradation rate experiment also showed clear utilization of protein-like DOM in both samples (Fig. 6b).

Naturally when assessing the composition and thus bioavailability

of rainwater DOM the primary source is important but subsequent atmospheric processing may play a major role in producing bioavailable DOC (Mead et al., 2013). Photochemistry has been shown to be able to increase the bioavailability of DOC in river water (Kieber et al., 1989; Miller et al., 1990; Moran and Zepp, 1997; Oberosterer and Benner, 2004; Tedetti et al., 2009). The significant correlation between BDOC and DOC concentrations also implies that they may be driven by a similar process or processes (Fig. 5). There is a greater blue-shifting (to shorter emission wavelengths) of the dominant A and C peaks in our EEM results, which is indicative of lower molecular weight compounds and general exposure of atmospheric aerosols to photo-oxidation processes that would act to decrease aromatic structures and unsaturated bonds (Graber and Rudich, 2006; Mladenov et al., 2012). Secondary organic aerosols formed by the oxidation of volatile organic compounds are also an important component in atmospheric DOC (Altieri et al., 2009; Miyazaki et al., 2007; Putman et al., 2012; Wozniak et al., 2014), however, whether they are bioavailable is currently not clear, and merits further study.

BDOC concentration also showed a dilution effect (Fig. 4), suggesting that BDOC was part of the DOC that is washed out of the atmosphere, while the insignificant correlation between BDOC% and rainfall amount indicates that bioavailable organic carbon (OC) may have similar water solubility to the refractory fraction and thus in the process of precipitation, both bioavailable and refractory OC are washed out from the atmosphere with no selective fractionation.

Interestingly, rainwater with all four types of back trajectories all showed high relative BDOC%. A potential reason behind the high bioavailability in all four types of back trajectories is that they all contain bioavailable organic matter that is from primary emission and/or resultant from atmospheric processing. A lower BDOC% was apparent in winter samples and this may be related to its source. As mentioned above, in winter the pollution from northern China contains a large amount of fossil fuel derived organic matter, which likely impacts bioavailability (Fig. 3).

4.3. Degradation rates of rainwater DOC

The first order degradation of rainwater DOC observed in our study (Fig. 6) is in agreement with previous studies on other aquatic ecosystems (Hung et al., 2003; Lønborg et al., 2010; Obernosterer and Benner, 2004). The degradation rate of the two rainwater samples examined here was higher than past studies on fluvial samples (Fellman et al., 2014; Fellman et al., 2009; Spencer et al., 2015), and similar to values reported from highly bioavailable permafrost thaw DOC (Mann et al., 2015; Spencer et al., 2015). The DOC loss rate decreased over time (Fig. 6a), consistent with previous studies on rainwater and river water (Avery et al., 2003; Hopkinson et al., 1997).

The high degradation rate of rainwater DOC implies that rain provides a potentially high bioavailability source of DOC to the surface ocean. In this study, the degradation rate of sample #49 was much lower than #48. Substrate DOC concentration has been shown to be important in determining degradation rate constants (Lønborg et al., 2010) along with other factors such as the microbial community structure, and nutrient availability (Lønborg et al., 2010; Letscher et al., 2015). The initial DOC concentration in #48 is much higher than in #49 (330 vs. 160 uM), which likely explains the difference in degradation rate. However, what role bacteria play in the degradation process in these two experiments is unclear, e.g. how the bacterial community composition factors into degradation kinetics during incubation is unknown and would provide fertile ground for future studies.

4.4. Ramifications of the high bioavailability of rainwater DOC

The flux of rainwater DOC to Xiamen Bay ($2.1\,g\,C\,m^{-2}\,yr^{-1}$) is similar to the median value reported for precipitation inputs to coastal

and island areas (Iavorivska et al., 2016), while the flux of BDOC to the adjacent coastal bay in Xiamen ($1.0\,g\,C\,m^{-2}\,yr^{-1}$) is very close to the precipitation input to the Long Bay ($1.3\,g\,C\,m^{-2}\,yr^{-1}$) (Avery et al., 2003). Recent studies have shown that on an annual basis approximately 14 Gg of DOC is exported to Xiamen Bay from the Jiulong River (Yang et al., 2013b), and the BDOC discharged by the Jiulong River is approximately 2.8 Gg yr^{-1} (total DOC flux multiplied by the average BDOC% of the river water (20%, Yang et al., 2013a)). Therefore, even though the rainwater DOC flux to Xiamen Bay is much smaller than the riverine DOC flux, the rainwater delivered approximately 35% of the riverine BDOC load to Xiamen Bay due to the high bioavailability of the rainwater DOC. These results highlight the importance of rainwater in providing BDOC to the ocean, and suggest the urgent need for more case studies, especially in the open ocean.

5. Implications and concluding remarks

Rainwater DOC may be an important contributor with respect to its role in supplying bioavailable DOC to receiving waters. In this study, we found that rainwater DOC concentration was highly variable at one single location and was significantly affected by rainfall amount and back trajectories (terrestrial vs. maritime). The average BDOC% was approximately 50% and showed high values from both terrestrial and maritime air masses. The input of BDOC to the coastal bay adjacent to Xiamen was estimated at approximately 35% of the riverine DOC flux, highlighting the significance of precipitation in supplying bioavailable DOC to the coastal ocean.

Recent studies in the northeastern United States found that the contribution of rainwater DOC was comparable to that of riverine DOC fluxes in inland watersheds (Iavorivska et al., 2017) and atmospheric deposition plays an important role in supplying biostable DOC (dissolved black carbon) to both river water and the ocean carbon pool (Jones et al., 2017; Bao et al., 2017). It is also evident from our biodegradation experiment that humic-like fluorescent DOM was produced and accumulated in the course of the 28 day bioincubations (Fig. 6c). This implies that microbial degradation of rainwater DOC could produce more stable DOC, which may contribute to the ocean microbial carbon pump, and thus long-term carbon storage (Jiao et al., 2010). Due to the very limited number of case studies to-date, there is currently no estimate of global atmospheric deposition of BDOC to the ocean. However, the high BDOC% in our study and in past studies (Avery et al., 2003; Godoy-Silva et al., 2017), implies that the atmospheric BDOC flux has potential ramifications for the global carbon cycle. Therefore, we suggest that future studies, especially in the open ocean (no data is available to date) are urgently required to better derive flux estimates for this term.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marchem.2018.07.008.

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