

RESEARCH ARTICLE

10.1029/2021JD034590

Key Points:

- Correlation coefficient and the ratio of dissolved black carbon to water-soluble organic carbon are relatively high for biomass burning aerosols
- Atmospheric deposition flux of dissolved black carbon to the ocean is mainly contributed by biomass burning aerosols
- The dissolved black carbon in aerosols has less condensed aromatic structures than the major rivers of the world

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

G. Zhong,
gczhong@gig.ac.cn

Citation:






Geng, X., Zhong, G., Liu, J., Sun, Y., Yi, X., Bong, C. W., et al. (2021). Year-round measurements of dissolved black carbon in coastal Southeast Asia aerosols: Rethinking its atmospheric deposition in the ocean. *Journal of Geophysical Research: Atmospheres*, 126, e2021JD034590. <https://doi.org/10.1029/2021JD034590>

Received 17 JAN 2021
Accepted 30 AUG 2021

Author Contributions:

Conceptualization: Xiaofei Geng, Guangcai Zhong
Data curation: Xiaofei Geng, Junwen Liu, Gan Zhang
Formal analysis: Xiaofei Geng, Guangcai Zhong
Funding acquisition: Gan Zhang
Investigation: Xiaofei Geng, Guangcai Zhong, Chui Wei Bong, Mohamad Pauzi Zakaria, Yan Ouyang
Methodology: Xiaofei Geng, Guangcai Zhong, Yue Sun, Xin Yi, Chui Wei Bong, Mohamad Pauzi Zakaria, Örjan Gustafsson
Project Administration: Gan Zhang
Resources: Xiaofei Geng, Junwen Liu, Chui Wei Bong, Mohamad Pauzi Zakaria, Örjan Gustafsson

Year-Round Measurements of Dissolved Black Carbon in Coastal Southeast Asia Aerosols: Rethinking Its Atmospheric Deposition in the Ocean

Xiaofei Geng^{1,2,3} , Guangcai Zhong^{1,3} , Junwen Liu⁴, Yue Sun^{1,3,5}, Xin Yi^{1,3,5}, Chui Wei Bong^{6,7}, Mohamad Pauzi Zakaria⁶ , Örjan Gustafsson⁸ , Yan Ouyang², and Gan Zhang^{1,3} 

¹State Key Laboratory of Organic Geochemistry, and Guangdong-Hong Kong-Macao Joint Laboratory for Environmental Pollution and Control, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, ²Nanjing Institute of Environmental Sciences, Ministry of Ecology and Environment of the People's Republic of China, Nanjing, China, ³CAS Center for Excellence in Deep Earth Science, Guangzhou, China, ⁴Institute for Environmental and Climate Research, Jinan University, Guangzhou, China, ⁵University of Chinese Academy of Sciences, Beijing, China, ⁶Institute of Ocean and Earth Sciences (IOES), University of Malaya, Kuala Lumpur, Malaysia, ⁷Institute of Biological Sciences, University of Malaya, Kuala Lumpur, Malaysia, ⁸Department of Environmental Science, Stockholm University, Stockholm, Sweden

Abstract Dissolved black carbon (DBC) is an important recalcitrant fraction of marine dissolved organic matter. Riverine discharge is the largest known source of oceanic DBC; however, the significance of atmospheric deposition as a source of oceanic DBC remains poorly understood. In this study, year-round aerosol sampling was carried out at a rural coastal site in Southeast Asia for DBC analysis using the benzene polycarboxylic acid (BPCA) method. The results revealed the uncertainty of an earlier estimate of the atmospheric deposition flux of DBC to the global ocean (F_{DBC}), which assumed a linear correlation between DBC and water-soluble organic carbon (WSOC). The correlation between DBC and WSOC depended on the sources of carbonaceous aerosols. The DBC/WSOC ratios were higher for the biomass burning aerosols. DBC was linearly correlated with black carbon (BC) for biomass or fossil fuel combustion aerosols. However, the DBC/BC ratios were higher for biomass burning aerosols (0.41 ± 0.22), whereas lower for fossil fuel combustion aerosols (0.04 ± 0.03). F_{DBC} was revisited based on the relationship between DBC and BC. F_{DBC} is primarily contributed by biomass burning aerosols and maybe previously underestimated. In this study, the DBC in aerosols had less condensed aromatic structures than the DBC present in the major rivers of the world, as shown by the BPCA compositions. This indicated that oceanic DBC sourced from atmospheric deposition was less likely to be removed by photodegradation and sedimentation, as compared to the DBC sourced from riverine discharge.

Plain Language Summary Understanding the sources and environmental processes of dissolved black carbon (DBC) in the ocean is crucial because it helps determine the quantity of DBC in the ocean that will finally transform into CO_2 , thereby affecting the atmospheric CO_2 stock and climate. The annual amount of DBC entering the ocean through atmospheric deposition (F_{DBC}) was previously estimated based on a linear correlation between DBC and water-soluble organic carbon (WSOC) in aerosols. In the present study, the correlation between DBC and WSOC was observed to be different for aerosols from various sources, such as biomass and fossil fuel combustion. The DBC/WSOC ratios were higher for biomass-burning aerosols. DBC/black carbon (BC) ratios were also higher for biomass burning aerosols, whereas lower for fossil fuel combustion aerosols. A new estimate of F_{DBC} was proposed, based on the relationship between DBC and BC, where F_{DBC} was primarily contributed by biomass-burning aerosols. DBC entering the ocean through atmospheric deposition had less condensed aromatic structures, as compared to DBC entering the ocean via rivers. This suggested that the former were less likely to be removed by photodegradation and sedimentation.

1. Introduction

Black carbon (BC) is an important form of refractory carbon. Atmospheric BC is produced by both biomass and fossil fuel combustion (Bond et al., 2013; Gustafsson et al., 2009), whereas global storage of BC

Software: Xiaofei Geng

Supervision: Guangcai Zhong, Gan Zhang

Validation: Xiaofei Geng

Visualization: Xiaofei Geng, Guangcai Zhong

Writing – original draft: Xiaofei Geng

Writing – review & editing: Xiaofei Geng, Guangcai Zhong, Chui Wei Bong, Mohamad Pauzi Zakaria, Örjan Gustafsson, Gan Zhang

is predominantly from biomass burning, which tends to reside in soils and aquatic environments, such as the ocean (Bird et al., 2015). BC formed by biomass burning was considered to be inert and represent a net sink of atmospheric CO₂ in earlier studies (Kuhlbusch, 1995; Seiler & Crutzen, 1980). However, increasing evidence shows that the composition and degradation potential of BC vary depending on the temperature at which BC is formed, the organic precursors burned, and the time consumed (Elmquist et al., 2006; Keiluweit et al., 2010; Zimmerman, 2010). As BC is aged in the environment, it becomes more abundant with oxygenated functional groups (e.g., hydroxyl, carbonyl, and carboxyl) and becomes more water-soluble (Roebuck et al., 2017).

A large portion of BC is delivered in the dissolved phase to the ocean by global rivers (i.e., DBC), making the ocean an important DBC reservoir (Coppola & Druffel, 2016; Dittmar & Paeng, 2009; Fang et al., 2021; Jaffe et al., 2013). DBC is also an important recalcitrant fraction of marine dissolved organic matter (DOM). Riverine discharge is the largest known source of DBC in the ocean (Jaffe et al., 2013; Jones et al., 2020). In addition to riverine discharge, there are other sources of oceanic DBC, such as atmospheric deposition, hydrothermal vents, and submarine groundwater discharge (Bao et al., 2017; Dittmar & Koch, 2006; Seidel et al., 2014). It is critical to constrain these sources to fully understand the environmental stability/recalcitrance of DBC and the cycling of BC.

Recently, the presence of DBC in aerosols from Chinese coastal seas and the northwestern Pacific was studied, and the atmospheric deposition flux of DBC to the global oceans (F_{DBC}) was estimated based on an observed linear relationship between DBC and water-soluble organic carbon (WSOC) (Bao et al., 2017). However, the linear relationship between the DBC and WSOC requires further verification. Although both DBC and WSOC are the components of carbonaceous aerosols, the abundance of DBC and WSOC is not always consistent. Carbonaceous aerosols are released by various sources including biomass burning, fossil fuel combustion, dust, biogenic sources, and secondary sources, such as the transformation from volatile organic compounds during atmospheric transport (Cong et al., 2015; Liu et al., 2014; Zhang et al., 2014). DBC is the carbon of water-soluble polycyclic aromatics (Dittmar, 2008). Combustion aerosols contain various polycyclic aromatics (Lin et al., 2018; Samburova et al., 2016). DBC may exist in fresh combustion aerosols and can be formed by oxidation of water-insoluble polycyclic aromatics in combustion aerosols during atmospheric transport (Keyte et al., 2013). DBC is also present in soil dust (Bao et al., 2017). WSOC occurs not only in combustion aerosols and soil dust, but also in biogenic aerosols and secondary organic aerosols transformed from VOCs (O'Dowd et al., 2004; Rinaldi et al., 2010). Therefore, the correlation between DBC and WSOC may depend on the source of carbonaceous aerosols.

To test this hypothesis, a year-round aerosol sampling was carried out at a rural coastal site in Southeast Asia to investigate the correlation between DBC and WSOC over a long duration, in which sources of carbonaceous aerosols varied. The DBC in aerosols was quantified using a molecular marker, namely benzene polycarboxylic acid (BPCA), method, which is the most widely used method for DBC quantification (Bao et al., 2017; Coppola & Druffel, 2016; Dittmar, 2008; Jaffe et al., 2013; Khan et al., 2016; Ziolkowski & Druffel, 2010). In addition to the quantification of DBC, this method provides information on the degree of aromatic condensation of DBC (Wiedemeier et al., 2015; Ziolkowski & Druffel, 2010), which is closely related to the extent of certain removal processes of DBC in the ocean, such as sedimentation and photodegradation (Stubbins et al., 2012; Xu et al., 2017). Field studies on aerosol DBC are sparse, and the differences in the molecular structures of aerosol DBC and riverine DBC are poorly understood.

In this study, we verified the hypothesis that the correlation between DBC and WSOC depends on the sources of carbonaceous aerosols. Furthermore, an alternative approach was proposed to estimate F_{DBC} . The different degrees of aromatic condensation (and hence removal efficiency) of oceanic DBC contributed by atmospheric deposition and riverine discharge were investigated using the BPCA method. Based on these results, new insights into the significance of atmospheric deposition as a source of oceanic DBC were provided.

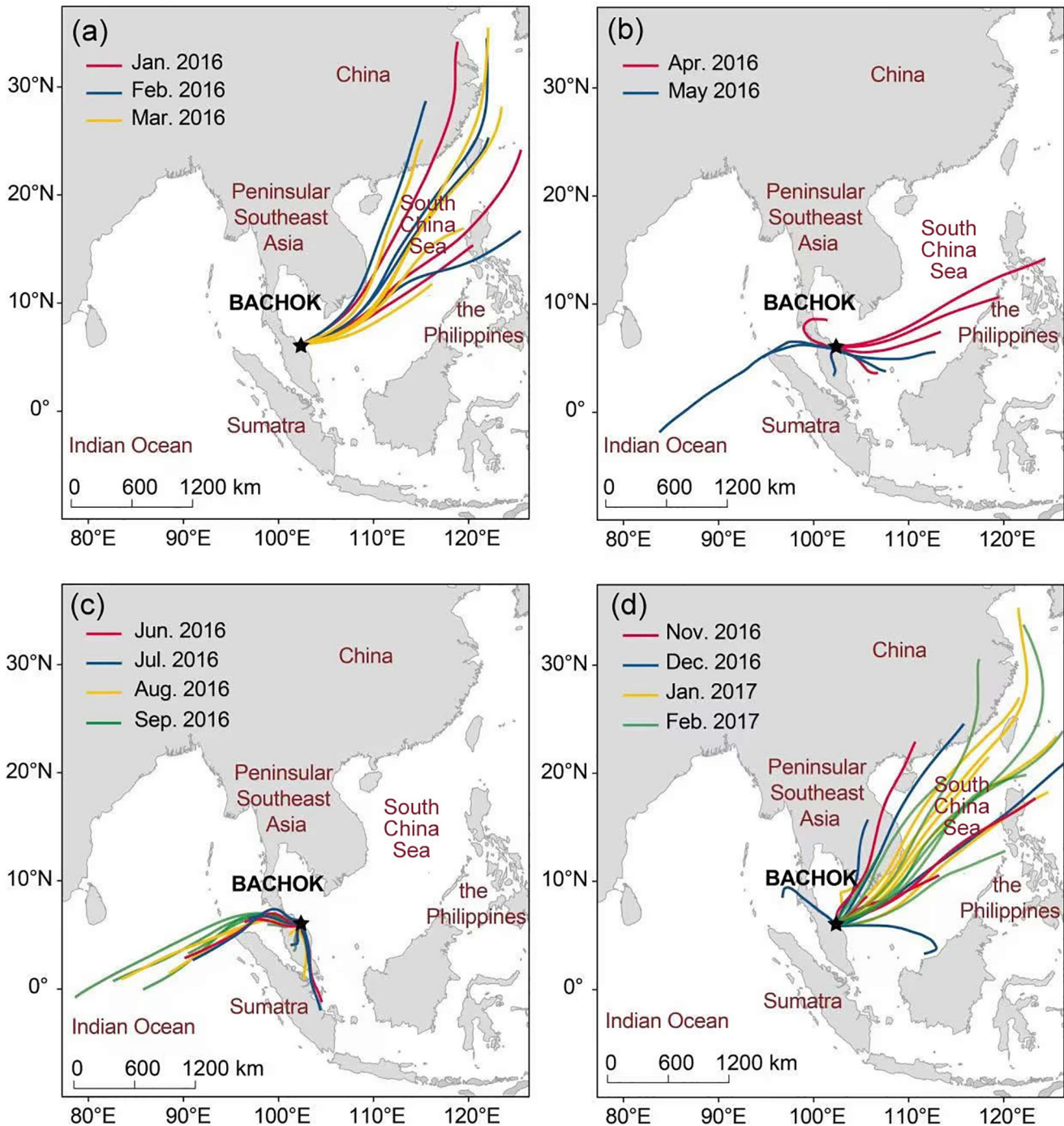


Figure 1. Location of the sampling site at Bachok, Kelantan State, Malaysia (black star), and the clustered 5-day air mass back trajectories arriving at the sampling site (1 m above ground level) for individual months from January 2016 to February 2017.

2. Data and Methods

2.1. Aerosol Sampling

Fifty-four aerosol samples were collected at the Bachok Marine Research Station (6.008°N, 102.425°E, Figure 1) from January 2016 to February 2017. The sampling site is located in a rural area of Kelantan State, situated on the east coast of Peninsular Malaysia. It is located <100 m from the South China Sea. Bachok

has an area of 280 km² and a population of 130,000. It has a tropical climate with annual mean temperatures of 25–35°C, and it experiences northeast monsoon in winter and southwest monsoon in summer (Figure 1).

Carbonaceous aerosols were collected on quartz fiber filters (QFF, 8 × 10 inches, PALL, the US) using a high-volume PM_{2.5} sampler (model: XT-1025, XTrust Instruments, China), which is commonly used in monitoring of carbonaceous aerosols (Liu et al., 2014; Wang et al., 2015; Zhang et al., 2014). The QFFs and the aluminum foils those were used for wrapping the QFFs were pre-baked at 500°C for 6 h before sampling to minimize organic residues. The air sampler was operated at a flow rate of 1,000 L min⁻¹ for approximately 24 h to collect aerosol samples. The QFFs those were loaded with aerosols were wrapped in pre-baked aluminum foils after sampling and stored in ziplock bags at –20°C, prior to analysis. In Southeast Asia, biomass burning is intensive during springtime and is a significant source of carbonaceous aerosols in this region. The original sampling plan was to collect aerosol samples more frequently during springtime (March–May, one sample every three days) and less frequently during other seasons (one sample per week). However, due to the heavy rain events or the breakdown of the sampler, sample numbers were less than expected in February and September, and no sample was obtained in October. The sampling dates for all aerosol samples are detailed in Table S1.

2.2. Chemical Analysis

The analyzed components of carbonaceous aerosols included DBC, WSOC, organic carbon (OC), BC, and anhydrosugars. In this study, OC, BC, and anhydrosugars were also analyzed for source identification of carbonaceous aerosols. Anhydrosugars are produced during the pyrolysis of cellulose. They are widely used as indicators of biomass burning aerosols (Jiang et al., 2018; Sullivan et al., 2014). Similar to DBC, BC is also produced during the combustion of organic matter; it is a refractory carbonaceous component with highly condensed aromatic structures and is insoluble in water and organic solvents (Bird et al., 2015; Bond et al., 2013). Its occurrence in ambient aerosols has been widely studied because of its ability to absorb sunlight and affect radiative forcing (Bond et al., 2013; B. Chen et al., 2013; Liu et al., 2020). In addition to BC, carbonaceous aerosols consist of OC. Similar to WSOC, OC can not only be released directly from biomass burning, fossil fuel combustion, and biogenic sources, but also be transformed from other organic compounds during atmospheric transport (Pio et al., 2011; Ram & Sarin, 2011; Rinaldi et al., 2010). WSOC is a subfraction of OC, and DBC is a subfraction of WSOC.

2.2.1. Analysis of DBC and Anhydrosugars

Two punches (45 mm diameter) of the QFF samples were extracted ultrasonically for 20 min with 30 mL of ultrapure water and repeated three times. Before extraction, 800 ng ¹³C₆-levoglucosan was added as a surrogate to check the recoveries of anhydrosugars, including levoglucosan, galactosan, and mannosan. The extracts were combined and filtered with a punch (20 mm diameter) of a glass fiber filter (0.45 μm pore size, 47 mm diameter, Whatman, the UK). DBC was isolated from the filtrate by solid phase extraction (SPE), which is the most common technique for DBC isolation from aquatic samples (Dittmar, 2008; Ziolkowski & Druffel, 2010). The filtrate was acidified with hydrochloric acid to pH 2, before passing it through a Bond Elut PPL (1 g, 6 mL, Agilent, the US) SPE cartridge preconditioned with 3 mL methanol and equilibrated with 3 mL hydrochloric acid (pH = 2). The solution that was passed through the SPE cartridge was freeze-dried to further analyze anhydrosugars (Fraction_{anhydrosugars}). The DBC adsorbed by the SPE cartridge was eluted with 6 mL of methanol. The eluate was transferred into an ampoule and dried at 50°C under high-purity nitrogen blowing for further analysis of DBC (Fraction_{DBC}).

To analyze Fraction_{DBC} using the BPCA method, 2 mL of nitric acid (65%, Sigma-Aldrich, the US) was added to the ampoule. The ampoule was sealed and heated to 180°C for 8 h in stainless-steel reaction vessels, following the method prescribed by Zhong et al. (2019); then, the DBC was oxidized to BPCAs. After oxidation, nitric acid was dried under high-purity nitrogen at 50°C. The dried samples were re-dissolved in 200 μL ultrapure water, followed by filtration with a syringe filter (13 mm × 0.22 μm, PTFE, ANPEL, China). BPCAs in the samples were separated with an Agilent InfinityLab Poroshell 120 SB-C18 (4.6 × 100 mm, 2.7 μm, the US) column and quantified by a high-performance liquid chromatography system equipped with a photodiode array detector (HPLC-PAD, Shimadzu, Japan) (Wiedemeier et al., 2016). Seven BPCAs were quantified, including 1,2,3,4,5,6-benzenhexacarboxylic acid (B6CA), 1,2,3,4,5-benzenepentacarboxylic acid (B5CA),

1,2,4,5-benzenetetracarboxylic acid, 1,2,3,5-benzenetetracarboxylic acid, 1,2,3,4-benzenetetracarboxylic acid (B4CAs), 1,2,3-benzenetricarboxylic acid, and 1,2,4-benzenetricarboxylic acid (B3CAs). Moreover, DBC concentrations were converted from the concentrations of BPCAs, based on an algorithm proposed by Dittmar (2008).

Fraction_{anhydrosugars} were spiked with methyl- β -D-xylopyranoside (in methanol) as an internal standard for the quantification of anhydrosugars. Then, the samples were dried under high-purity nitrogen flow. They were derivatized at 70°C for 1 h after the addition of 200 μ L N,O-bis-trimethylsilyl-trifluoroacetamide (1% trimethylchlorosilane) and 100 μ L anhydrous pyridine. After derivatization, the samples were dried by blowing high-purity nitrogen and re-dissolving it in 500 μ L of hexane. The amounts of anhydrosugars, their internal standards, and surrogates were obtained by the quantification of their trimethylsilyl derivatives using gas chromatography-mass spectrometry. The details of the instrumental analysis of anhydrosugars can be found in Jiang et al. (2018).

2.2.2. Analysis of WSOC, OC, and BC

Two punches (45 mm in diameter) of the QFF samples were extracted ultrasonically with 40 mL of ultrapure water for 30 min. The extract was then passed through a syringe filter (25 mm diameter, 0.22 pore size, PTFE, ANPEL, China). The concentration of WSOC was quantified as dissolved organic carbon in the filtrate using a high-temperature catalytic oxidation instrument (Vario TOC cube, Elementar, Germany) following the non-purgeable OC protocol (Witkowska & Lewandowska, 2016).

OC and BC on the QFF samples were quantified using the thermal-optical technique, which is currently the most widely used technique for the quantification of OC and BC in atmospheric aerosols. The QFF samples were acidified by fumigation with >37% hydrochloric acid in open glass Petri dishes placed in a desiccator for 24 h to remove carbonates and were subsequently dried at 60°C for 1 h to remove any remaining hydrochloric acid. A 1.5 cm² piece filter was cut out from each QFF sample and used to analyze OC and BC with a thermal-optical transmittance (TOT) carbon analyzer (Sunset Laboratory, the US) following the NIOSH 5040 protocol (B. Chen et al., 2013). The method of OC and BC analysis is well-established and quality-assured (B. Chen et al., 2013; Liu et al., 2020). The instrument was calibrated using a standard sucrose solution prior to each analysis. During the analysis, OC was volatilized from the particulate carbon on the filter in a stepped-temperature program in a helium atmosphere. BC was volatilized from the remaining particulate carbon on the filter in the following stepped-temperature program in 10% oxygen in a helium atmosphere. The volatilized OC (or BC) was further oxidized to carbon dioxide and monitored using a nondispersive infrared detector to quantify OC (or BC).

2.2.3. Data Quality

Three to four field blanks and replicate samples were analyzed for DBC, anhydrosugars, WSOC, OC, and BC. The blanks of DBC, anhydrosugars, OC, and BC were negligible (<5% of levels in samples). Although the blanks of WSOC were $33 \pm 13\%$ of the samples' WSOC amounts, they represented a relatively stable background level (coefficient of variation: 7%, $n = 4$). The concentrations of WSOC in the samples were blank-corrected. WSOC levels in these coastal aerosols were relatively low. Larger sample sizes are recommended to be extracted for WSOC analysis of coastal and marine aerosols in the future to reduce the percentages of WSOC blanks. The recovery of ¹³C₆-levoglucosan was $74 \pm 7\%$. The concentrations of anhydrosugars were recovery-corrected. The coefficients of variation of replicated concentrations ($n = 4$) were 15%, 6%, 3%, 0.4%, and 2.9% for DBC, anhydrosugars, WSOC, OC, and BC, respectively.

2.3. Air Mass Back Trajectories and Fire Counts

Air mass back trajectories and fire counts were also analyzed for the source identification of carbonaceous aerosols. Air mass back trajectories demonstrate the regions where the air masses pass through before they arrive at a sampling site. They were used to investigate the transport pathways of carbonaceous aerosols and understand the influence of atmospheric transport on the sources of carbonaceous aerosols. Fire counts reveal the frequencies of open biomass burning in a region. They were used to investigate the influence of biomass burning on carbonaceous aerosols of our sampling site.

2.3.1. Air Mass Back Trajectories

Air mass back trajectories were calculated using the hybrid single-particle Lagrangian integrated trajectory (HYSPLIT) model provided by the Air Resources Laboratory (ARL) of NOAA (<http://ready.arl.noaa.gov/HYSPLIT.php>). The gridded meteorological data that were used in the HYSPLIT model were obtained from the GDAS 1° archive provided by the ARL (www.ready.noaa.gov/archives.php). The residence time of carbonaceous aerosols was estimated to be 3–8 days in some studies (Rasch et al., 2001; Reddy & Venkataraman, 1999). Three-day or 5-day or 7-day air mass back trajectories were often calculated using the HYSPLIT model to investigate the transport pathways of carbonaceous aerosols (Cong et al., 2015; Liu et al., 2014; Zhang et al., 2014).

In this study, 5-day back trajectories of the air masses arriving at the sampling site were generated at intervals of 6 h from January 1, 2016 to February 28, 2017. The arrival height of the air masses was set to 1 m above ground level. Approximately 120 trajectories were generated for each month. The air mass back trajectories for each month were needed for the source identification of carbonaceous aerosols. To simplify the air mass back trajectory results, the generated trajectories of each month were clustered using the HYSPLIT model and represented by a few mean trajectories calculated by the model. The number of mean trajectories was set to the value beyond which the standard change in the total spatial variance increased drastically (criterion: 30%). In this study, the number of mean trajectories generated for each month was three to five (Figure 1).

2.3.2. Fire Counts

The fire counts were acquired from the Visible Infrared Imaging Radiometer Suite (VIIRS) 375 m active fire product (<https://firms.modaps.eosdis.nasa.gov/map>), whose data were obtained from the VIIRS sensor aboard the joint NASA/NOAA Suomi National Polar-orbiting Partnership (Suomi NPP) and NOAA-20 satellites. The VIIRS 375 m active fire product provides fire hotspot counts within a 0.25×0.25 grid size.

3. Results and Discussion

3.1. Sample Classification by Sources of Carbonaceous Aerosols

To test our hypothesis that the correlation between DBC and WSOC depends on the sources of carbonaceous aerosols, the samples were classified into groups according to the sources of carbonaceous aerosols. Biomass burning aerosols are expected to be significant in springtime, as biomass burning in Southeast Asia is intensive during this period. The sampling site receives air masses from the northern part of Southeast Asia and East Asia due to the northeast monsoon and from the southern part of Southeast Asia due to the southwest monsoon. The different atmospheric transport pathways in the two monsoon seasons may result in different sources of carbonaceous aerosols. Therefore, the classification of aerosol samples was carried out according to the biomass burning and monsoon seasons, the durations of which were determined based on the results of fire counts and air mass back trajectories, respectively. The differences in the sources of carbonaceous aerosols among the classified groups were verified using chemical analyses.

From April–May 2016, heavy open biomass burning occurred locally, as revealed by the results of the fire counts (Figure 2). As the sampling site was located in Kelantan State, which is one of the main agricultural regions in Malaysia, biomass burning was likely related to agricultural activities. Local open biomass burning occurred less frequently during other months (Figure 2). Therefore, aerosol samples collected during April–May 2016 were grouped together, as they were significantly influenced by biomass burning aerosols. The aerosol samples obtained at other times were further classified into groups, depending on the monsoon. The results of air mass back trajectories showed that the sampling site was influenced by the northeast monsoon during January–March 2016, by the southwest monsoon during June–September 2016, and by the northeast monsoon from November 2016 to February 2017 (Figure 1). Aerosol samples collected during these three periods were included in individual groups. The differences in sources of carbonaceous aerosols among the four classified sample groups, namely the samples obtained during January–March 2016, April–May 2016, June–September 2016, and November 2016–February 2017, were verified by chemical analysis results, as discussed below.

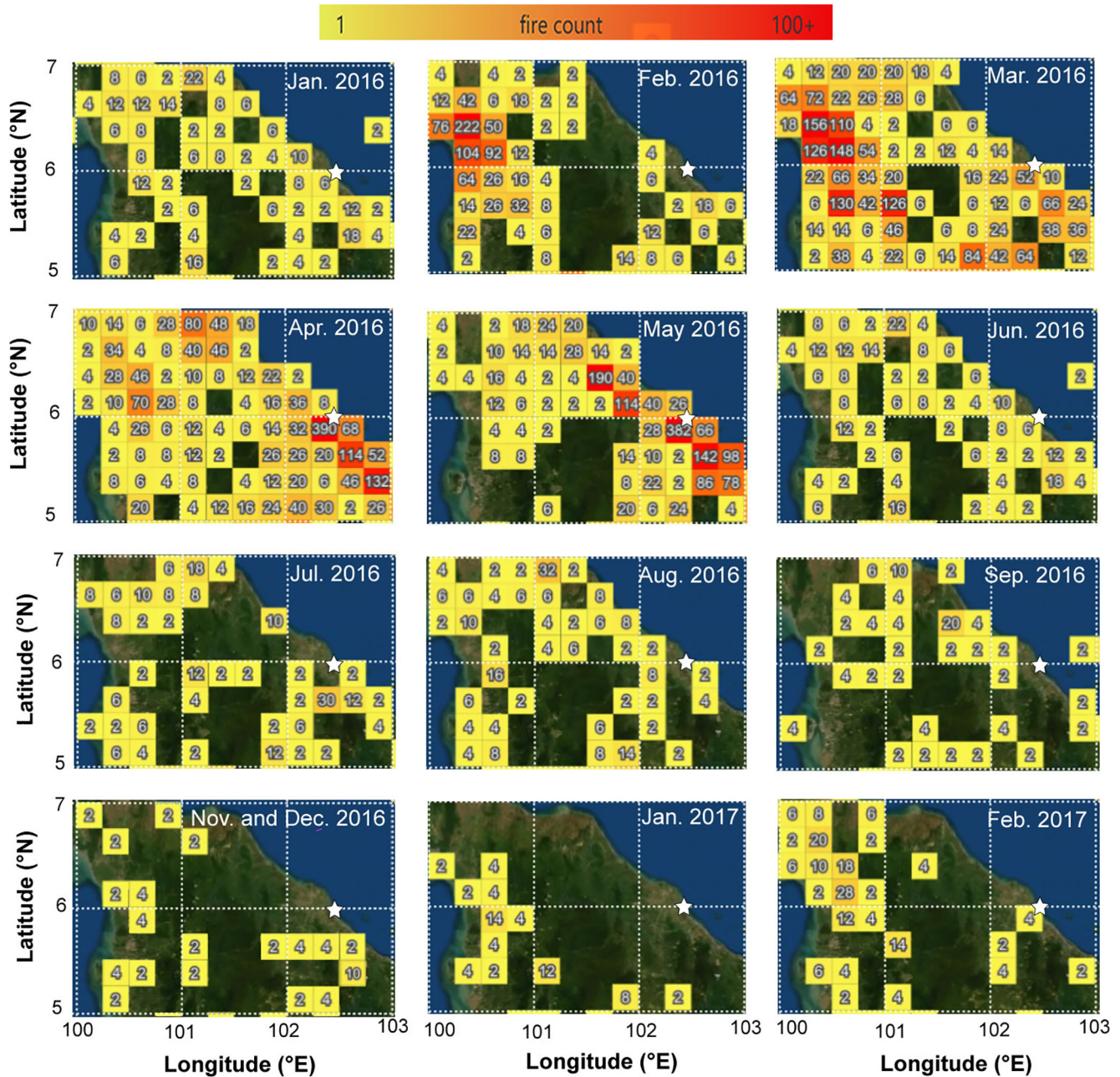


Figure 2. Fire counts of northern Peninsular Malaysia from January 2016 to February 2017. The white star shows the location of the sampling site at Bachok, Kelantan State, Malaysia. The numbers in the grids represent the fire counts of the grids.

For samples collected during April–May 2016 (group “BB”), the predominant source of carbonaceous aerosols was biomass burning. The biomass burning-tracing anhydrosugars were more abundant in this group of samples (Figure 3e). Increased air concentrations of other carbonaceous components, including DBC, WSOC, and OC were also observed (Figures 3a–3c), suggesting heavy aerosol pollution caused by biomass burning during this period. The high OC/BC ratios further indicated the significance of biomass burning aerosols during April–May 2016 (Figure 3f), given that high OC/BC ratios are generally found in biomass burning aerosols (Y. Chen & Xie, 2014), whereas low OC/BC ratios are typically found in fossil fuel smoke and urban aerosols (Pio et al., 2011).

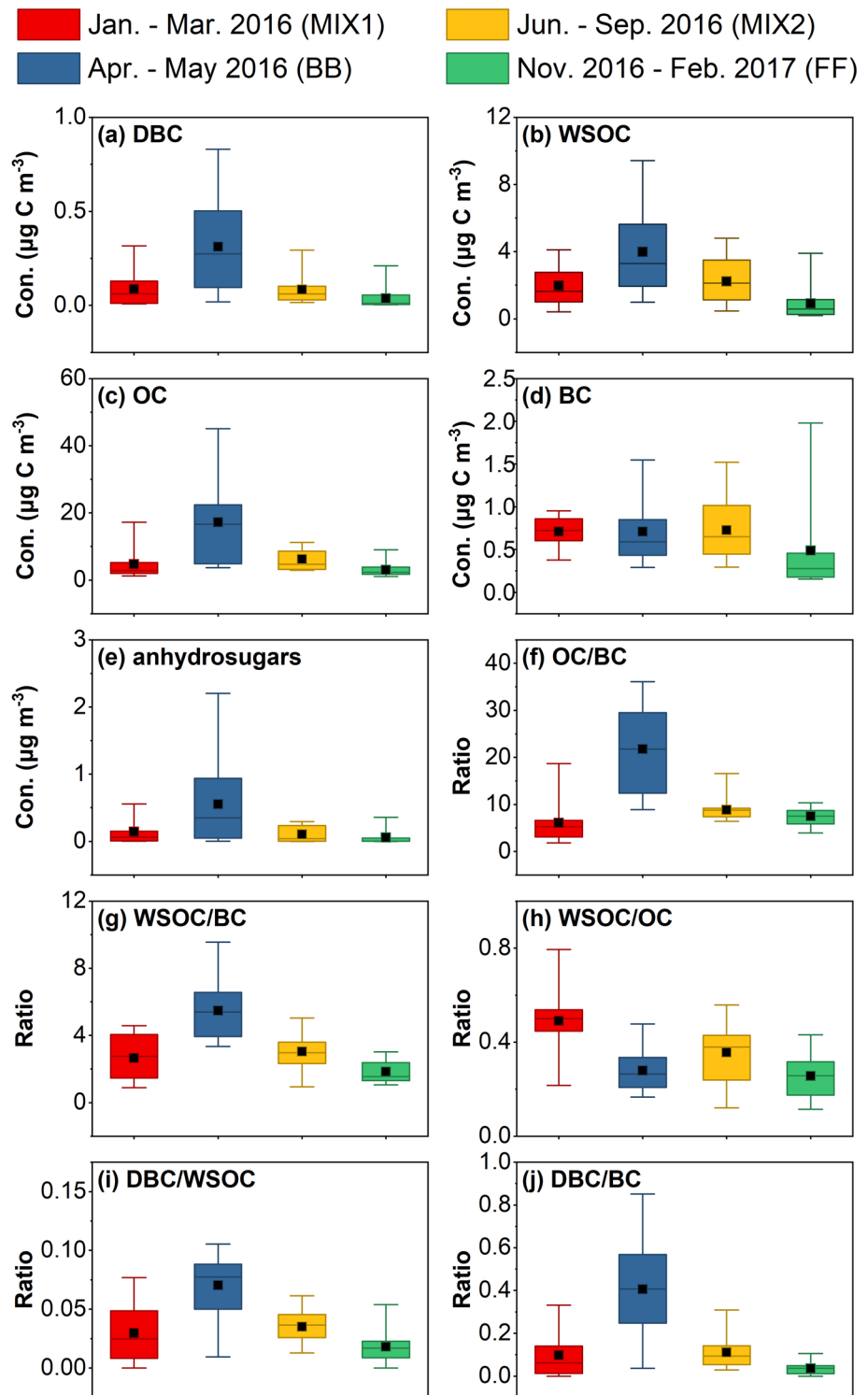


Figure 3. Concentrations (Con., a–e) and ratios (f–j) of carbonaceous components for different sample groups. “BB,” “FF,” and “MIX1” (or “MIX2”) indicate sample groups primarily influenced by biomass burning, fossil fuel combustion, and mixed sources, respectively.

Table 1
R Values of Pearson Correlation Between DBC and Other Carbonaceous Components for Different Sample Groups (MIX1, BB, MIX2, and FF)

	MIX1 (n = 10)	BB (n = 15)	MIX2 (n = 15)	FF (n = 14)
WSOC	0.84 ^a	0.97 ^a	0.88 ^a	0.98 ^a
OC	0.44	0.92 ^a	0.50	0.95 ^a
Anhydrosugars	0.11	0.78 ^a	0.49	--
BC	0.51	0.87 ^a	0.53 [*]	0.94 ^a

^a $p < 0.01$; ^{*} $p < 0.05$; --: no result because data of anhydrosugars did not follow a normal distribution; MIX1 and MIX2: sample groups primarily influenced by mixed sources of carbonaceous aerosols; BB and FF: sample groups primarily influenced by biomass burning and fossil fuel combustion aerosols, respectively.

For samples obtained from November 2016 to February 2017 (group “FF”), the source of carbonaceous aerosols was primarily fossil fuel combustion. The samples in this group exhibited a distinguishing characteristic of low WSOC/BC ratios (Figure 3g), which is generally observed for urban aerosols (Ho et al., 2006; Park & Cho, 2011). Open biomass burning was the least frequent during this period, as indicated by the fire counts (Figure 2). The levels of biomass burning-tracing anhydrosugars were also low from November 2016 to February 2017 (Figure 3e). Therefore, biomass burning was insignificant during this period.

Carbonaceous aerosols were generally contributed by mixed sources in January–March 2016 (group “MIX1”) and June–September 2016 (group “MIX2”). These samples did not show distinguishing characteristics of biomass or fossil fuel combustion aerosols (i.e., group “BB” and “FF,” Figure 3). It is established that high WSOC/OC ratios are indicators of secondary organic aerosols (Kondo et al., 2007; Ram & Sarin, 2011). Higher WSOC/OC ratios were observed in samples that were affected by mixed

sources of carbonaceous aerosols (i.e., group “MIX1” and “MIX2”), as compared to the samples that were primarily affected by biomass or fossil fuel combustion aerosols (i.e., group “BB” and “FF,” Figure 3h). This indicated the significance of secondary organic aerosols for certain samples of group “MIX1” and “MIX2.” Backward trajectories showed that air masses arriving at the sampling site passed over Peninsular Southeast Asia and southern China from January to March of 2016 and passed over Peninsular Malaysia and Sumatra from June to September of 2016 (Figure 1). During the long-range atmospheric transport from these potential source regions to our sampling site, the oxidation of volatile or water-insoluble compounds could be significant enough to form WSOC, leading to increased WSOC/OC ratios.

The differences in the sources of carbonaceous aerosols among the four classified groups were also supported by the results of a recent study on BC source apportionment based on radiocarbon analysis, using samples from the same sample archive as this study (Liu et al., 2020). Specifically, the contributions of biomass burning to BC were generally higher for the samples of group “BB”; the contributions of fossil fuel combustion to BC were generally higher for the samples of group “FF”; the contributions of biomass burning and fossil fuel combustion to BC were similar for samples of group “MIX1” and “MIX2” (Liu et al., 2020).

3.2. Source-Dependence of DBC–WSOC Correlations

The results of linear correlation between DBC and WSOC for the different sample groups were in accordance with our hypothesis that the relationship between DBC and WSOC depends on the sources of carbonaceous aerosols. Strong linear correlations were observed for sample groups predominantly influenced by combustion sources (i.e., group “BB” or “FF,” $r \geq 0.97$, $p < 0.01$, Table 1, Figure S1); however, the mean DBC/WSOC ratio was significantly higher for group “BB” samples (0.070 ± 0.025), as compared to “FF” samples (0.023 ± 0.014 , Figure 3i). The linear correlations between DBC and WSOC were evidently weaker for sample groups influenced by mixed sources (i.e., $r = 0.84$ for group “MIX1” and $r = 0.88$ for “MIX2,” $p < 0.01$, Table 1, Figure S1). This may be because the DBC/WSOC ratios were relatively different for samples affected by biomass and fossil fuel combustion sources, or because biogenic and secondary sources could have contributed to WSOC but not DBC. The DBC/WSOC ratios of groups “MIX” samples ranged between the DBC/WSOC ratios of group “BB” and “FF” samples. Thus, both linear correlations and ratios between the DBC and WSOC depended on the sources of carbonaceous aerosols.

These results suggested uncertainty in the current estimate of F_{DBC} , assuming a linear relationship between DBC and WSOC (Bao et al., 2017). A strong linear relationship between DBC and WSOC was observed for aerosols collected from China’s coastal seas and the northwestern Pacific Ocean in this previous study ($r = 0.99$, $p < 0.001$) (Bao et al., 2017), in which the mean DBC/WSOC ratio (0.028 ± 0.014) was as low as the mean DBC/WSOC ratio of group “FF” samples in our study. This strong linear relationship and low DBC/WSOC ratio may be attributed to fossil fuel combustion sources, as biomass burning was not prevalent in China (an important source region) during the sampling period of the study (i.e., late March to early May) (J. Chen et al., 2017).

3.3. Toward a Better Estimate of F_{DBC}

Correlations between DBC and other widely studied carbonaceous components (i.e., anhydrosugars, OC, and BC) were investigated to get a better estimate of F_{DBC} . The linear correlations between DBC and other carbonaceous components were significant for group “BB” and “FF” samples (r : 0.78 to 0.98, $p < 0.01$) whereas insignificant for group “MIX1” and “MIX2” samples (Table 1). Therefore, DBC levels cannot be simply estimated based on a linear relationship between the DBC and these carbonaceous components. The insignificant correlations between DBC and OC for group “MIX1” and “MIX2” samples might be due to the contributions of biogenic or secondary sources to OC but not to DBC. Anhydrosugars are products of biomass burning; however, they are not produced by fossil fuel combustion and non-combustion sources. This could explain the insignificant correlations between DBC and anhydrosugars for group “MIX1” and “MIX2” samples.

The correlations between DBC and the biomass-burning tracing anhydrosugars were relatively weaker than those between DBC and other components, even when local biomass burning was apparent (Table 1). There are several possible reasons for this result. First, the anhydrosugars/WSOC ratio can vary by magnitude depending on the biofuel type (Sullivan et al., 2014). This might be similar for the anhydrosugars/DBC ratio, considering the highly correlated DBC and WSOC concentrations for biomass burning aerosols. Second, biomass burning produces both anhydrosugars and DBC; however, the burning conditions that favor the formation of the two chemicals are different. A lower burning temperature benefits the formation of chemicals without condensed aromatic structures, such as anhydrosugars, whereas high burning temperature favors the formation of condensed aromatic structures, such as DBC (Bird et al., 2015). Third, the different extent of degradation between DBC and anhydrosugars in the air could also be a reason (Hennigan et al., 2010; Hoffmann et al., 2010).

Evidently, DBC/BC ratios were higher for group “BB” samples (0.41 ± 0.22) and lower for group “FF” samples (0.04 ± 0.03), although correlations between DBC and BC were strong for both groups (r : 0.87 and 0.94, $p < 0.01$, Table 1). The DBC/BC ratios for group “MIX1” and “MIX2” samples lay between those of group “BB” and “FF” samples (Figure 3j), likely due to a mixing effect of biomass burning and fossil fuel combustion aerosols. The different DBC/BC ratios of group “BB” and “FF” samples might be due to different burning conditions of biomass and fossil fuel. BC is not a pure chemical but a combustion continuum, composed of materials ranging from slightly charred fuel to highly condensed aromatic rings, such as soot (Elmquist et al., 2006). In this study, the TOT method for quantifying BC has been widely used in atmospheric science research, and the BC determined by this method is typically interchangeable with soot (Petzold et al., 2013). Generally, biomass burning occurs at lower temperatures, favoring the formation of less-condensed aromatic structures, such as DBC, whereas fossil fuel combustion occurs at a higher temperature, favoring the formation of highly condensed aromatic structures, such as soot (Bird et al., 2015). This mechanism can be further supported by the distribution of BC in the four sample groups. Although there was a conspicuous increase in other carbonaceous components, including DBC, WSOC, OC, and anhydrosugars for biomass burning aerosols (i.e., group “BB” samples), an increase in BC was not observed (Figures 3a–3e).

In this study, an estimate of F_{DBC} was made, based on the linear relationships between DBC and BC observed for biomass burning and fossil fuel combustion aerosols. The atmospheric deposition flux of BC to global oceans (F_{BC}) was 12 Tg yr^{-1} , as reported in a previous study (Jurado et al., 2008). Globally, biomass burning and fossil fuel combustion have been estimated to contribute $\sim 60\%$ and $\sim 40\%$ of BC to the atmosphere, respectively (Bond et al., 2013). The contributions of biomass burning and fossil fuel combustion to F_{BC} ($F_{\text{BC-BB}}$ and $F_{\text{BC-FF}}$) were also assumed to be 60% and 40% (equal to 7.2 and 4.8 Tg yr^{-1}), respectively. F_{DBC} from biomass burning ($F_{\text{DBC-BB}}$) was calculated based on the linear relationship between DBC and BC of biomass burning aerosols observed in this study (Figure 4a). The intercept of the linear regression between DBC and BC of biomass burning aerosols could be regarded as zero considering the co-emissions of DBC and BC. The slope of the linear regression was 0.563 ± 0.232 (99% confidence interval, $r^2 = 0.752$, $p < 0.001$), so DBC/BC was 0.563 ± 0.232 . Thus, $F_{\text{DBC-BB}}$ was equal to $F_{\text{BC-BB}}$ times 0.563 ± 0.232 , and its value was $4.054 \pm 1.670 \text{ Tg yr}^{-1}$. Similarly, F_{DBC} due to fossil fuel combustion ($F_{\text{DBC-FF}}$) was calculated using the observed linear relationship between the DBC and BC of fossil fuel combustion aerosols (Figure 4b). The slope of the linear regression between DBC and BC of fossil fuel combustion aerosols was 0.100 ± 0.031 (99%

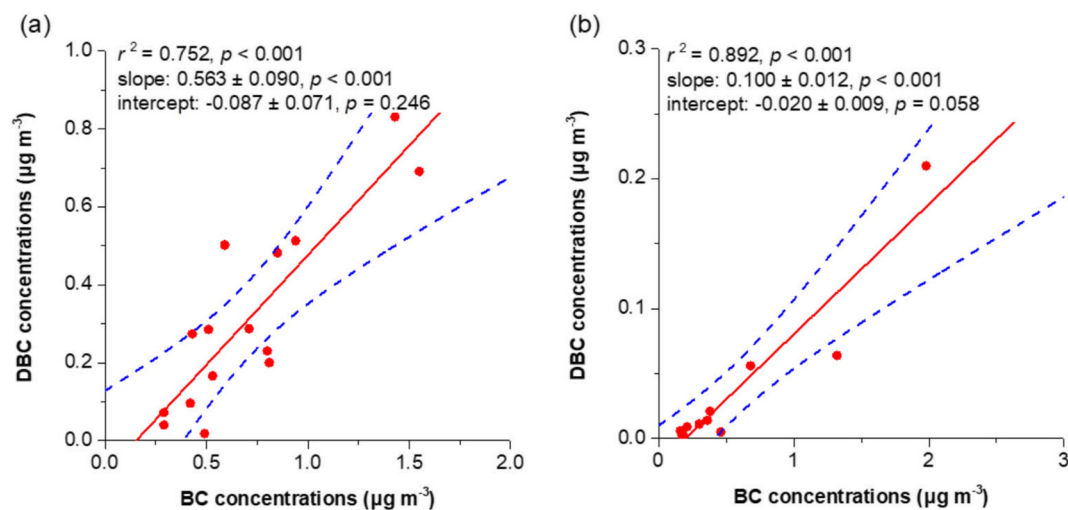


Figure 4. Linear regressions between dissolved black carbon and black carbon for sample groups primarily influenced by biomass burning (a) and fossil fuel combustion (b). Area between the dashed lines shows the 99% confidence interval of the linear regression.

confidence interval, $r^2 = 0.892, p < 0.001$). Therefore, $F_{\text{DBC-FF}}$ was equal to $F_{\text{BC-FF}}$ times 0.100 ± 0.031 , and its value was $0.480 \pm 0.149 \text{ Tg yr}^{-1}$. F_{DBC} was the sum of $F_{\text{DBC-BB}}$ and $F_{\text{DBC-FF}}$, which was $4.534 \pm 1.819 \text{ Tg yr}^{-1}$.

Further studies are required to obtain a more accurate value of F_{DBC} . There was uncertainty in the current estimate of atmospheric BC contributed by biomass burning and fossil fuel combustion (Bond et al., 2013). The value of F_{BC} in the literature was calculated based on BC concentrations measured via remote sensing method, which was different from the one used to quantify BC in this study (Jurado et al., 2008); thus, this also contributed to F_{DBC} uncertainty. Transformation of DBC from water-insoluble polycyclic aromatics during atmospheric transport from coastal regions to the open ocean may take place (Keyte et al., 2013), but this process is currently poorly understood. It resulted in higher DBC/BC ratios and an underestimate of F_{DBC} in this study. Dust was suggested to be another source of DBC in marine aerosols (Bao et al., 2017). The aerosols we analyzed were atmospheric fine particles ($\text{PM}_{2.5}$). Dust generally has a larger particle size (Kirillova et al., 2014), so it was not discussed in the present study. F_{DBC} in our study would be further underestimated because a calculation of dust DBC deposition flux was not included. The atmospheric deposition flux of dust to the ocean has been estimated in several studies since 2000, and it varies from 294 to 478 Tg yr^{-1} (Mahowald et al., 2005). BC contents in typical arable soils (top soils) have been reported to be less than 3 g kg^{-1} (Brodowski et al., 2007; Lehndorff et al., 2014). If the BC contents in the dust are assumed to be 3 g kg^{-1} and the dust BC is fully oxidized to DBC during atmospheric transport, the atmospheric deposition of dust DBC to the ocean is $0.882\text{--}1.434 \text{ Tg yr}^{-1}$. Actually, global dust emissions are mainly from arid regions (Mahowald et al., 2005). Lower BC contents in the soils of these regions are expected.

3.4. Aromatic Condensation of Aerosol DBC

To fully understand the significance of atmospheric deposition as a source of oceanic DBC, it is necessary to understand F_{DBC} and aromatic condensation of aerosol DBC. This is because the stability (or residence time) of DBC in the ocean is closely related to the aromatic condensation of DBC. DBC with more condensed aromatic structures is prone to removal from seawater by photodegradation and adsorption onto sinking particles (Stubbins et al., 2012; Xu et al., 2017).

BPCA composition can be an indicator of the aromatic condensation of DBC. The enrichment of BPCAs with three and four carboxylic groups (B3CAs and B4CAs) shows DBCs with less condensed aromatic systems (Wiedemeier et al., 2015; Ziolkowski & Druffel, 2010). In this study, B3CAs and B4CAs in aerosols accounted for $76.9 \pm 9.7\%$ of BPCAs (Table S2 and Figure 5). These percentages were higher than the available data for DBC in rivers and coastal waters (Ding et al., 2013; Dittmar, 2008; Roebuck et al., 2018) but similar to those for DBC in surface or deep seawater in remote oceans (i.e., the Arctic, Atlantic, and Pacific oceans)

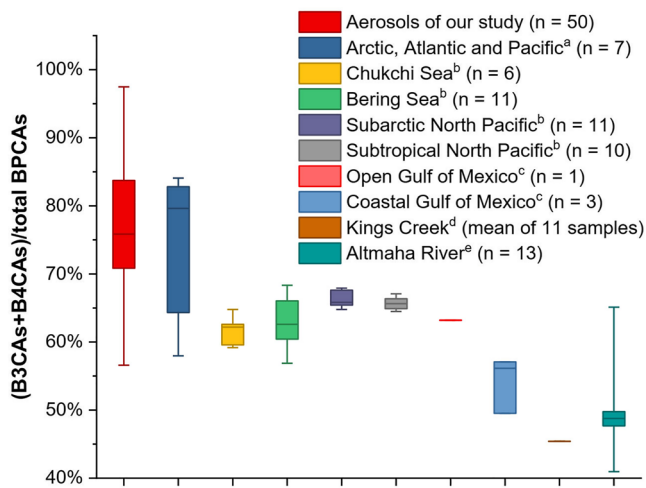


Figure 5. Percentages of B3CAs and B4CAs derived from the dissolved black carbon of aerosols in this study and from the waters of the Arctic, Atlantic, and Pacific oceans; open and coastal Gulf of Mexico; and Kings Creek and Altamaha River in the United States. References: ^a(Coppola & Druffel, 2016), ^b(Nakane et al., 2017), ^c(Dittmar, 2008), ^d(Ding et al., 2013), and ^e(Roebeck et al., 2018).

(Coppola & Druffel, 2016; Nakane et al., 2017) (Figure 5). A recent study reported that the B6CA/B5CA ratios were higher for DBC in the major rivers of the world than for oceanic DBC (Wagner et al., 2019). All these BPCA compositions suggested that aerosol DBC was relatively condensed as oceanic DBC but less condensed than DBC in the major rivers of the world. Thus, oceanic DBC sourced from atmospheric deposition was less likely to be removed by photodegradation and sedimentation compared to DBC sourced from riverine discharge.

4. Conclusions and Perspectives

This year-round study at a well-positioned Southeast Asia coastal observatory revealed that the relationship between aerosol DBC and WSOC depended on the sources of carbonaceous aerosols. It suggested the uncertainty of the previous estimate of F_{DBC} , which assumed a single linear relationship between DBC and WSOC. An alternative approach to estimate F_{DBC} was proposed based on the linear relationships between the DBC and BC of biomass and fossil fuel combustion aerosols.

Atmospheric deposition, as a source of DBC in the ocean, may be more important than previously considered. The new estimate of F_{DBC} in this study ($4.534 \pm 1.819 \text{ Tg yr}^{-1}$) was higher than that reported in a previous study ($1.8 \pm 0.83 \text{ Tg yr}^{-1}$) (Bao et al., 2017); moreover, it was 12%–45% of the global riverine flux of DBC to the ocean ($18 \pm 4 \text{ Tg yr}^{-1}$) (Jones

et al., 2020). Aerosol DBC was less condensed than the DBC of the major rivers of the world, as revealed by the BPCA compositions in the present study. This suggested that oceanic DBC from atmospheric deposition was less likely to be removed by sedimentation and photodegradation, as compared to that from riverine discharge. The importance of atmospheric deposition becomes more pertinent when considering the different removal efficiencies in seawater for DBC sourced from atmospheric deposition against riverine discharge. A recent study found that oceanic DBC was $\sim 6\%$ enriched in $\delta^{13}\text{C}$, as compared to DBC exported by major rivers (-24% vs. -30%); it proposed a non-riverine source of oceanic DBC (Wagner et al., 2019). The non-riverine source remains unknown, and the present results demonstrated that atmospheric deposition was a candidate.

Atmospheric deposition may contribute to a DBC pool with a younger ^{14}C age in the surface ocean. Radiocarbon analysis has great potential in the study of the cycling timescale of DOC and DBC in the ocean (Coppola & Druffel, 2016; Ziolkowski & Druffel, 2010). A DBC pool in the surface ocean has been found to be over 10,000 years of ^{14}C age younger than the DBC pool in the deep ocean (Coppola & Druffel, 2016). Previous studies have also found a younger pool of DOC in the surface ocean, which is attributed to labile DOC from primary production at the surface (Druffel et al., 1992; Williams & Druffel, 1987). This mechanism cannot explain the two DBC pools because DBC is combustion-derived. Biomass burning was estimated to contribute to approximately 90% of F_{DBC} in our study. This contribution should be even higher in the pre-industrial era. DBC of biomass burning aerosols has a modern ^{14}C age (Liu et al., 2014; Zhang et al., 2014). Thus, atmospheric deposition introduces DBC with a younger ^{14}C age into the surface ocean and should be a contributor of the younger DBC pool in the surface ocean.

Further studies are required to reduce the uncertainty of F_{DBC} and to quantitatively understand the different removal efficiencies of oceanic DBC from atmospheric deposition and riverine discharge, to fully understand the significance of atmospheric deposition as a source of oceanic DBC. Additionally, ^{13}C and ^{14}C analyses of DBC in marine aerosols can be carried out in the future to verify the influence of atmospheric deposition on the carbon isotope signatures of DBC in the ocean.

Data Availability Statement

Data of fire counts are assessable from NASA's FIRMS (<https://firms.modaps.eosdis.nasa.gov/map>). Experimental data of this study will be archived using the Harvard Dataverse (<https://dataverse.harvard.edu/>). They are uploaded temporarily in the Supporting Information S1. The archiving will be finished before the study is published.

Acknowledgments

This work is funded by the Natural Science Foundation of China (No. 41430645 and 41877349), the International Partnership Program of Chinese Academy of Sciences (132744KYSB20170002), the State Key Laboratory of Organic Geochemistry, GIGCAS (No. SKLOG2020-3 and SKLOG-201744), the Guangdong Foundation for Program of Science and Technology Research (No.2019B121205006), the Ministry of Higher Education Malaysia (HICoE Phase II Fund, grant IOES-2014D), the Swedish Research Foundation Vinnova through grant VINNMER Marie Curie Incoming Fellow (2016–04077) as well as the Swedish Research Council (VR) project (# 2015–03279) and a VR Distinguished Professorship Grant to Ö.G. (# 2017-01601). The authors gratefully acknowledge the China-Sri Lanka Joint Center for Education and Research, Chinese Academy of Sciences for supporting in the international collaboration in this work. We thank Tingting Li for her assistance in the laboratory work. Data of air mass backward trajectories were generated by the HYSPLIT transport and dispersion model (<https://ready.arl.noaa.gov/HYSPLIT.php>).

References

- Bao, H., Niggemann, J., Luo, L., Dittmar, T., & Kao, S. J. (2017). Aerosols as a source of dissolved black carbon to the ocean. *Nature Communications*, 8(1), 510. <https://doi.org/10.1038/s41467-017-00437-3>
- Bird, M., Wynn, J. G., Saiz, G., Wurster, C. M., & McBeath, A. (2015). The pyrogenic carbon cycle. *Annual Review of Earth and Planetary Sciences*, 43(1), 273–298. <https://doi.org/10.1146/annurev-earth-060614-105038>
- Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Bernsten, T., DeAngelo, B. J., et al. (2013). Bounding the role of black carbon in the climate system: A scientific assessment. *Journal of Geophysical Research - D: Atmospheres*, 118(11), 5380–5552. <https://doi.org/10.1002/jgrd.50171>
- Brodowski, S., Amelung, W., Haumaier, L., & Zech, W. (2007). Black carbon contribution to stable humus in German arable soils. *Geoderma*, 139(1–2), 220–228. <https://doi.org/10.1016/j.geoderma.2007.02.004>
- Chen, B., Andersson, A., Lee, M., Kirillova, E. N., Xiao, Q., Kruså, M., et al. (2013). Source forensics of black carbon aerosols from China. *Environmental Science and Technology*, 47(16), 9102–9108. <https://doi.org/10.1021/es401599r>
- Chen, J., Li, C., Ristovski, Z., Milic, A., Gu, Y., Islam, M. S., et al. (2017). A review of biomass burning: Emissions and impacts on air quality, health and climate in China. *The Science of the Total Environment*, 579, 1000–1034. <https://doi.org/10.1016/j.scitotenv.2016.11.025>
- Chen, Y., & Xie, S.-d. (2014). Characteristics and formation mechanism of a heavy air pollution episode caused by biomass burning in Chengdu, Southwest China. *The Science of the Total Environment*, 473, 507–517. <https://doi.org/10.1016/j.scitotenv.2013.12.069>
- Cong, Z., Kang, S., Kawamura, K., Liu, B., Wan, X., Wang, Z., et al. (2015). Carbonaceous aerosols on the south edge of the Tibetan Plateau: Concentrations, seasonality and sources. *Atmospheric Chemistry and Physics*, 15(3), 1573–1584. <https://doi.org/10.5194/acp-15-1573-2015>
- Coppola, A. I., & Druffel, E. R. M. (2016). Cycling of black carbon in the ocean. *Geophysical Research Letters*, 43(9), 4477–4482. <https://doi.org/10.1002/2016gl068574>
- Ding, Y., Yamashita, Y., Dodds, W. K., & Jaffe, R. (2013). Dissolved black carbon in grassland streams: Is there an effect of recent fire history? *Chemosphere*, 90(10), 2557–2562. <https://doi.org/10.1016/j.chemosphere.2012.10.098>
- Dittmar, T. (2008). The molecular level determination of black carbon in marine dissolved organic matter. *Organic Geochemistry*, 39(4), 396–407. <https://doi.org/10.1016/j.orggeochem.2008.01.015>
- Dittmar, T., & Koch, B. P. (2006). Thermogenic organic matter dissolved in the abyssal ocean. *Marine Chemistry*, 102(3–4), 208–217. <https://doi.org/10.1016/j.marchem.2006.04.003>
- Dittmar, T., & Paeng, J. (2009). A heat-induced molecular signature in marine dissolved organic matter. *Nature Geoscience*, 2(3), 175–179. <https://doi.org/10.1038/ngeo440>
- Druffel, E. R., Williams, P. M., Bauer, J. E., & Ertel, J. R. (1992). Cycling of dissolved and particulate organic matter in the open ocean. *Journal of Geophysical Research*, 97(C10), 15639–15659. <https://doi.org/10.1029/92jc01511>
- Elmqvist, M., Cornelissen, G., Kukulska, Z., & Gustafsson, Ö. (2006). Distinct oxidative stabilities of char versus soot black carbon: Implications for quantification and environmental recalcitrance. *Global Biogeochemical Cycle*, 20(2). <https://doi.org/10.1029/2005GB002629>
- Fang, Y., Chen, Y. J., Huang, G. P., Hu, L. M., Tian, C. G., Xie, J. Q., et al. (2021). Particulate and dissolved black carbon in Coastal China Seas: Spatiotemporal variations, dynamics, and potential implications. *Environmental Science and Technology*, 55(1), 788–796. <https://doi.org/10.1021/acs.est.0c06386>
- Gustafsson, O., Krusa, M., Zencak, Z., Sheesley, R. J., Granat, L., Engstrom, E., et al. (2009). Brown clouds over South Asia: Biomass or fossil fuel combustion? *Science*, 323(5913), 495–498. <https://doi.org/10.1126/science.1164857>
- Hennigan, C. J., Sullivan, A. P., Collett, J. L., Jr, & Robinson, A. L. (2010). Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals. *Geophysical Research Letters*, 37(9), L06803. <https://doi.org/10.1029/2010gl043088>
- Ho, K., Lee, S., Cao, J., Li, Y., Chow, J. C., Watson, J. G., & Fung, K. (2006). Variability of organic and elemental carbon, water soluble organic carbon, and isotopes in Hong Kong. *Atmospheric Chemistry and Physics*. <https://doi.org/10.5194/acp-6-4569-2006>
- Hoffmann, D., Tilgner, A., Iinuma, Y., & Herrmann, H. (2010). Atmospheric stability of levoglucosan: A detailed laboratory and modeling study. *Environmental Science and Technology*, 44(2), 694–699. <https://doi.org/10.1021/es902476f>
- Jaffe, R., Ding, Y., Niggemann, J., Vahatalo, A. V., Stubbins, A., Spencer, R. G. M., et al. (2013). Global charcoal mobilization from soils via dissolution and riverine transport to the oceans. *Science*, 340(6130), 345–347. <https://doi.org/10.1126/science.1231476>
- Jiang, H., Zhong, G., Wang, J., Jiang, H., Tian, C., Li, J., et al. (2018). Using polyurethane foam-based passive air sampling technique to monitor monosaccharides at a regional scale. *Environmental Science and Technology*, 52(21), 12546–12555. <https://doi.org/10.1021/acs.est.8b02254>
- Jones, M. W., Coppola, A. I., Santin, C., Dittmar, T., Jaffe, R., Doerr, S. H., & Quine, T. A. (2020). Fires prime terrestrial organic carbon for riverine export to the global oceans. *Nature Communications*, 11(1), 2791. <https://doi.org/10.1038/s41467-020-16576-z>
- Jurado, E., Dachs, J., Duarte, C. M., & Simó, R. (2008). Atmospheric deposition of organic and black carbon to the global oceans. *Atmospheric Environment*, 42(34), 7931–7939. <https://doi.org/10.1016/j.atmosenv.2008.07.029>
- Keiluweit, M., Nico, P. S., Johnson, M. G., & Kleber, M. (2010). Dynamic molecular structure of plant biomass-derived black carbon (bio-char). *Environmental Science and Technology*, 44(4), 1247–1253. <https://doi.org/10.1021/es9031419>
- Keyte, I. J., Harrison, R. M., & Lammel, G. (2013). Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons - A review. *Chemical Society Reviews*, 42(24), 9333–9391. <https://doi.org/10.1039/c3cs60147a>
- Khan, A. L., Jaffe, R., Ding, Y., & McKnight, D. M. (2016). Dissolved black carbon in Antarctic lakes: Chemical signatures of past and present sources. *Geophysical Research Letters*, 43(11), 5750–5757. <https://doi.org/10.1002/2016GL068609>
- Kirillova, E. N., Andersson, A., Han, J., Lee, M., & Gustafsson, O. (2014). Sources and light absorption of water-soluble organic carbon aerosols in the outflow from northern China. *Atmospheric Chemistry and Physics*, 14(3), 1413–1422. <https://doi.org/10.5194/acp-14-1413-2014>

- Kondo, Y., Miyazaki, Y., Takegawa, N., Miyakawa, T., Weber, R., Jimenez, J., et al. (2007). Oxygenated and water-soluble organic aerosols in Tokyo. *Journal of Geophysical Research*, *112*(D1). <https://doi.org/10.1029/2006jd007056>
- Kuhlbusch, T. A. J. (1995). Method for determining black carbon in residues of vegetation fires, *Environmental Science and Technology*, *29*(10), 2695–2702. <https://doi.org/10.1021/Es00010a034>
- Lehdorff, E., Roth, P. J., Cao, Z. H., & Amelung, W. (2014). Black carbon accrual during 2000 years of paddy-rice and non-paddy cropping in the Yangtze River Delta, China. *Global Change Biology*, *20*(6), 1968–1978. <https://doi.org/10.1111/gcb.12468>
- Lin, P., Fleming, L. T., Nizkorodov, S. A., Laskin, J., & Laskin, A. (2018). Comprehensive molecular characterization of atmospheric brown carbon by high resolution mass spectrometry with electrospray and atmospheric pressure photoionization. *Analytical Chemistry*, *90*(21), 12493–12502. <https://doi.org/10.1021/acs.analchem.8b02177>
- Liu, J., Andersson, A., Zhong, G., Geng, X., Ding, P., Zhu, S., et al. (2020). Isotope constraints of the strong influence of biomass burning to climate-forcing Black Carbon aerosols over Southeast Asia. *The Science of the Total Environment*, *744*, 140359. <https://doi.org/10.1016/j.scitotenv.2020.140359>
- Liu, J., Li, J., Zhang, Y., Liu, D., Ding, P., Shen, C., et al. (2014). Source apportionment using radiocarbon and organic tracers for PM_{2.5} carbonaceous aerosols in Guangzhou, South China: Contrasting local- and regional-scale haze events. *Environmental Science and Technology*, *48*(20), 12002–12011. <https://doi.org/10.1021/es503102w>
- Mahowald, N. M., Baker, A. R., Bergametti, G., Brooks, N., Duce, R. A., Jickells, T. D., et al. (2005). Atmospheric global dust cycle and iron inputs to the ocean. *Global Biogeochemical Cycle* *19*(4). <https://doi.org/10.1029/2004gb002402>
- Nakane, M., Ajioka, T., & Yamashita, Y. (2017). Distribution and sources of dissolved black carbon in surface waters of the Chukchi Sea, Bering Sea, and the North Pacific Ocean. *Frontiers in Earth Science-Switzerland*, *5*, 34. <https://doi.org/10.3389/feart.2017.00034>
- O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., et al. (2004). Biogenically driven organic contribution to marine aerosol. *Nature*, *431*(7009), 676–680. <https://doi.org/10.1038/nature02959>
- Park, S. S., & Cho, S. Y. (2011). Tracking sources and behaviors of water-soluble organic carbon in fine particulate matter measured at an urban site in Korea. *Atmospheric Environment*, *45*(1), 60–72. <https://doi.org/10.1016/j.atmosenv.2010.09.045>
- Petzold, A., Ogren, J. A., Fiebig, M., Laj, P., Li, S.-M., Baltensperger, U., et al. (2013). Recommendations for the interpretation reporting of "black carbon" measurements. *Atmospheric Chemistry and Physics*, *13*(16), 8365–8379. <https://doi.org/10.5194/acp-13-8365-2013>
- Pio, C., Cerqueira, M., Harrison, R. M., Nunes, T., Mirante, F., Alves, C., et al. (2011). OC/EC ratio observations in Europe: Re-thinking the approach for apportionment between primary and secondary organic carbon. *Atmospheric Environment*, *45*(34), 6121–6132. <https://doi.org/10.1016/j.atmosenv.2011.08.045>
- Ram, K., & Sarin, M. M. (2011). Day-night variability of EC, OC, WSO and inorganic ions in urban environment of Indo-Gangetic Plain: Implications to secondary aerosol formation. *Atmospheric Environment*, *45*(2), 460–468. <https://doi.org/10.1016/j.atmosenv.2010.09.055>
- Rasch, P. J., Collins, W. D., & Eaton, B. E. (2001). Understanding the Indian Ocean Experiment (INDOEX) aerosol distributions with an aerosol assimilation. *Journal of Geophysical Research*, *106*(D7), 7337–7355. <https://doi.org/10.1029/2000jd900508>
- Reddy, M. S., & Venkataraman, C. (1999). Direct radiative forcing from anthropogenic carbonaceous aerosols over India. *Current Science*, *76*(7), 1005–1011.
- Rinaldi, M., Decesari, S., Finessi, E., Giulianelli, L., Carbone, C., Fuzzi, S., et al. (2010). Primary and secondary organic marine aerosol and oceanic biological activity: Recent results and new perspectives for future studies. *Advanced Meteorology*, *2010*, 10. <https://doi.org/10.1155/2010/310682.2010>
- Roebuck, J. A., Medeiros, P. M., Letourneau, M. L., & Jaffé, R. (2018). Hydrological controls on the seasonal variability of dissolved and particulate black carbon in the Altamaha River, GA. *Journal of Geophysical Research- Biogeosciences*, *123*(9), 3055–3071. <https://doi.org/10.1029/2018jg004406>
- Roebuck, J. A., Podgorski, D. C., Wagner, S., & Jaffé, R. (2017). Photodissolution of charcoal and fire-impacted soil as a potential source of dissolved black carbon in aquatic environments. *Organic Geochemistry*, *112*, 16–21. <https://doi.org/10.1016/j.orggeochem.2017.06.018>
- Samburova, V., Connolly, J., Gyawali, M., Yatavelli, R. L. N., Watts, A. C., Chakrabarty, R. K., et al. (2016). Polycyclic aromatic hydrocarbons in biomass-burning emissions and their contribution to light absorption and aerosol toxicity. *The Science of the Total Environment*, *568*, 391–401. <https://doi.org/10.1016/j.scitotenv.2016.06.026>
- Seidel, M., Beck, M., Riedel, T., Waska, H., Suryaputra, I. G., Schnetger, B., et al. (2014). Biogeochemistry of dissolved organic matter in an anoxic intertidal creek bank. *Geochimica Cosmochimica Acta*, *140*, 418–434. <https://doi.org/10.1016/j.gca.2014.05.038>
- Seiler, W., & Crutzen, P. J. (1980). Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning. *Climatic Change*, *2*(3), 207–247. <https://doi.org/10.1007/bf00137988>
- Stubbins, A., Niggemann, J., & Dittmar, T. (2012). Photo-lability of deep ocean dissolved black carbon. *Biogeosciences*, *9*(5), 1661–1670. <https://doi.org/10.5194/bg-9-1661-2012>
- Sullivan, A., May, A., Lee, T., McMeeking, G., Kreidenweis, S., Akagi, S., et al. (2014). Airborne characterization of smoke marker ratios from prescribed burning. *Atmospheric Chemistry and Physics*, *14*, 10535–10545. <https://doi.org/10.5194/acp-14-10535-2014>
- Wagner, S., Brandes, J., Spencer, R. G. M., Ma, K., Rosengard, S. Z., Moura, J. M. S., & Stubbins, A. (2019). Isotopic composition of oceanic dissolved black carbon reveals non-riverine source. *Nature Communications*, *10*(1), 5064. <https://doi.org/10.1038/s41467-019-13111-7>
- Wang, F. W., Guo, Z. G., Lin, T., Hu, L. M., Chen, Y. J., & Zhu, Y. F. (2015). Characterization of carbonaceous aerosols over the East China Sea: The impact of the East Asian continental outflow. *Atmospheric Environment*, *110*, 163–173. <https://doi.org/10.1016/j.atmosenv.2015.03.059>
- Wiedemeier, D. B., Abiven, S., Hockaday, W. C., Keiluweit, M., Kleber, M., Masiello, C. A., et al. (2015). Aromaticity and degree of aromatic condensation of char. *Organic Geochemistry*, *78*, 135–143. <https://doi.org/10.1016/j.orggeochem.2014.10.002>
- Wiedemeier, D. B., Lang, S. Q., Gierga, M., Abiven, S., Bernasconi, S. M., Früh-Green, G. L., et al. (2016). Characterization, quantification and compound-specific isotopic analysis of pyrogenic carbon using benzene polycarboxylic acids (BPCA). *Journal of Visualised Experiments*, *111*. <https://doi.org/10.3791/53922>
- Williams, P. M., & Druffel, E. R. (1987). Radiocarbon in dissolved organic matter in the central North Pacific Ocean. *Nature*, *330*(6145), 246–248. <https://doi.org/10.1038/330246a0>
- Witkowska, A., & Lewandowska, A. U. (2016). Water soluble organic carbon in aerosols (PM₁, PM_{2.5}, PM₁₀) and various precipitation forms (rain, snow, mixed) over the southern Baltic Sea station. *The Science of the Total Environment*, *573*, 337–346. <https://doi.org/10.1016/j.scitotenv.2016.08.123>
- Xu, F., Wei, C., Zeng, Q., Li, X., Alvarez, P. J. J., Li, Q., et al. (2017). Aggregation behavior of dissolved black carbon: Implications for vertical mass flux and fractionation in aquatic systems. *Environmental Science and Technology*, *51*(23), 13723–13732. <https://doi.org/10.1021/acs.est.7b04232>

- Zhang, Y. L., Li, J., Zhang, G., Zotter, P., Huang, R. J., Tang, J. H., et al. (2014). Radiocarbon-based source apportionment of carbonaceous aerosols at a regional background site on Hainan Island, South China. *Environmental Science and Technology*, *48*(5), 2651–2659. <https://doi.org/10.1021/es4050852>
- Zhong, G., Sun, Y., Geng, X., Yi, X., & Zhang, G. (2019). Benzene polycarboxylic acid characterisation of polyaromatics in ambient aerosol: Method development. *Atmospheric Environment*, *211*, 55–62. <https://doi.org/10.1016/j.atmosenv.2019.04.057>
- Zimmerman, A. R. (2010). Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environmental Science and Technology*, *44*(4), 1295–1301. <https://doi.org/10.1021/es903140c>
- Ziolkowski, L. A., & Druffel, E. R. M. (2010). Aged black carbon identified in marine dissolved organic carbon. *Geophysical Research Letters*, *37*, Artn L1660110.