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Characterization of biogenic primary and secondary organic aerosols in the marine atmosphere over the East China Sea

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Abstract

Molecular composition and abundance of sugars and secondary organic aerosols (SOA) from biogenic sources over the East China Sea were investigated based on gas chromatography/mass spectrometry. Biogenic SOA tracers and sugars exhibit higher levels in the samples affected by continental air masses, suggesting the terrestrial outflows of organic matter to the East China Sea. Glucose was the dominant sugar species (0.31–209 ng m^{-3}, 18.8 ng m^{-3}), followed by mannitol – a fungal spore tracer. All sugar compounds showed higher concentrations in the nighttime than in the daytime. 3-Methyl-1,2,3-butanetricarboxylic acid, one high-oxidation tracer of monoterpene SOA, was found to be the most abundant species among measured biogenic SOA markers, suggesting the input of aged organic aerosols through long-range transport. Fungal-spore-derived organic carbon (OC) was the biggest contributor to total OC (0.03–19.8%, 3.1%), followed by sesquiterpene-derived secondary OC (SOC), biomass-burning-derived OC, monoterpene- and isoprene-derived SOC. Larger carbon percentages of biogenic OCs and SOCs in total OC presented in the terrestrially influenced aerosols indicate significant contributions of continental aerosols through long-range transport. Positive matrix factorization results illustrate that the secondary sulfate ammonia, secondary nitrate and biogenic SOA, sea salt and coal combustion were the main sources controlling the marine aerosols over the East China Sea, again highlighting the importance of Asian continent as a natural emitter of biogenic organic aerosols together with anthropogenic aerosols over the coastal marine atmosphere.

1 Introduction

Oceans cover more than 70% of the Earth's surface and marine aerosols contribute significantly to the global aerosol load (O'Dowd et al., 2004), playing an important role in the albedo, atmospheric processes, atmospheric chemistry, climate, and biogeochemical cycling of nutrients (O'Dowd and de Leeuw, 2007; Shi et al., 2011). Such influences depend on the chemical composition and concentrations of marine aerosols. In recent years, significant abundances of organic matter in marine aerosol and their importance to the cloud condensation nuclei (CCN) formation as well as their direct and indirect radiative effects have been reported (Tervahattu et al., 2002; O'Dowd et al., 2004; Facchini et al., 2008; Sciare et al., 2009; Pringle et al., 2010; Bougiatioti et al., 2011; Ovadnevaite et al., 2011a; Ovadnevaite et al., 2011b). However, information about marine organic aerosol remains poor owing to various emission sources, complex formation mechanisms, and limited field measurements regarding their chemical composition and concentrations (Cavalli et al., 2004; O'Dowd and de Leeuw, 2007). Therefore, it is necessary to investigate the loadings, molecular compositions and sources of marine organic aerosols, especially in coastal and offshore regions where the land/ocean interaction is active.

In general, sources of organic compounds in marine aerosols comprise natural and anthropogenic emissions. For example, surface-active organic matter of biogenic origin in the ocean (e.g. bacteria, viruses and detritus) can be transferred to the marine atmosphere by bubble-bursting processes (Gershey, 1983; Mochida et al., 2002; Sciare et al., 2009; Gantt and Meskhidze, 2013). Terrestrial air masses also bring plentiful organic matter derived from natural and/or anthropogenic activities to the oceanic atmosphere via long-range atmospheric transport (Zhou et al., 1990; Hawkins et al., 2010; Uematsu et al., 2010; Srinivas et al., 2011; Kumar et al., 2012; Kang et al., 2017). Sugars, important water-soluble organic constituents of atmospheric particulate matter, are substantial in both continental (Pashynska et al., 2002; Iinuma et al., 2007; Yttri et al., 2007; Fu et al., 2008; Jia and Fraser, 2011; Cong et al., 2015) and marine aerosols (Simoneit et al., 2004b; Fu et al., 2011). Due to their ubiquity and abundance, sugars can be used to elucidate sources and transport of atmospheric organic aerosols. Levoglucosan along with its two isomers, mannosan and galactosan, as the primary thermal alteration products by the pyrolysis of cellulose and hemicellulose, has been recognized as specific tracers for biomass burning (Simoneit, 2002). Trehalose is a recognized fungal carbohydrate, which can be indicative of soil dust (Feng and Simpson, 2007; Fu et al., 2012). Arabitol and mannitol are tracers for airborne fungal spores (Bauer et al., 2008). Sucrose could serve as a marker for airborne pollen grains (Pacini, 2000; Fu et al., 2012), while fructose and glucose can be emitted from plant pollen, fruits and detritus (Speranza et al., 1997; Baker et al., 1998; Pacini, 2000). These sugar compounds have been detected in some marine aerosols and effectively used as key tracers to assess contributions of different emission sources (Simoneit et al., 2004b). Despite their importance, the knowledge about molecular characterization of sugars in marine aerosols is still rare because of various sources and inconvenience of sampling.

Apart from primary sources, atmospheric volatile organic compounds (VOCs) emitted from ocean and/or continents also have significant impacts on marine aerosols. VOCs can react with oxidants, such as ozone (O_3), nitrogen oxides (NO_x) and OH radicals in the atmosphere, producing secondary organic aerosols (SOA) (Atkinson and Arey, 2003; Claeys et al., 2004a; Jaoui et al., 2005; Meskhidze and Nenes, 2006; Claeys et al., 2007; Hallquist et al., 2009; Gantt and Meskhidze, 2013; Hu et al., 2013). SOAs contribute substantially to atmospheric particulate OM and strongly affects the regional and global air quality, climate and human health (Zhu et al., 2016; Chen et al., 2017). Recent studies have revealed that SOA is an important or even the dominant contributor to $PM_{2.5}$ during heavy haze events in China (Cao et al., 2017). Due to poor understanding of sources and formation mechanisms of SOA, accurately measuring and modelling SOA concentrations remains a big issue (Zheng et al., 2017). It was reported that emissions of biogenic VOCs (BVOCs) were one order of magnitude larger than those of anthropogenic VOCs on a global scale (Guenther et al., 2006). BVOCs emitted from terrestrial vegetation include isoprene, monoterpenes and sesquiterpenes as well as other compounds (Guenther et al., 2006; Goldstein and Galbally, 2007), which could exert large impacts on marine aerosols through continental aerosols' outflow. On the other hand, marine phytoplankton and seaweeds can release isoprene and other BVOCs as well (Yokouchi et al., 1999; Shaw et al., 2010), especially during the phytoplankton blooms (Hu et al., 2013). Marine-derived SOAs by oxidation of phytoplankton-produced isoprene have been shown to remarkably influence the chemical composition of marine CNN and cloud droplet number, forming an indirect climatic effect (Meskhidze and Nenes, 2006; Gantt et al., 2009; Bikkina et al., 2014). In addition to isoprene, the photooxidation products of oceanic monoterpenes (e.g. α- and β-pinene) were established as well (Yassaa et al., 2008; Gantt et al., 2009; Fu et al., 2011). However, to date, the accurate molecular characterisation and spatial distribution of biogenic SOAs (BSOA) in the marine atmosphere are not well known due to their chemical complexity and process nonlinearity (Chen et al., 2017). Consequently, there remains an urgent need for studies about marine BSOA on a regional and/or global scale currently.

In this study, we investigated molecular compositions, abundances and spatial distributions of sugars and BSOA tracers in marine aerosols over the East China Sea (ECS), which is located between the east coast of Asian continent and the western North Pacific. The ECS is susceptible to the outflow of continental OM from natural and anthropogenic activities in the mainland. The contributions of secondary organic carbon (SOC) from isoprene, monoterpene and sesquiterpene to the total OC were estimated. Positive matrix factorization (PMF) was also used to estimate the contributions of sources identified by biomass burning tracers (e.g.

levoglucosan), primary saccharides including fungal spore and pollen tracers, BSOA tracers from oxidation of BVOCs, inorganic ions and some other reliable source markers.

2 Materials and methods

2.1 Aerosol sampling

Marine total suspended particles (TSP) were collected during May 18 to June 12, 2014. The sampling was performed using a high-volume air sampler (Kimoto, Japan) at an airflow rate of 0.8 m^3 min^{-1} on board of the KEXUE-1 Research Vessel during a National Natural Science Foundation of China (NSFC) sharing cruise. Figure 1 shows the cruise tracks and concentrations of chlorophyll-a over the ECS. Detailed sampling information and map of sampling sites are described elsewhere (Kang et al., 2017).

2.2 Organic species analysis

Filter aliquots were ultrasonically extracted for 10 min three times using dichloromethane/methanol mixture (2:1, v/v). The solvent extracts were filtered through quartz wool packed in a Pasteur pipette and concentrated with a rotary evaporator, and then blown down to dryness with pure nitrogen gas. The extracts were reacted with 50 µL of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylsilyl chloride and 10 µL of pyridine at 70°C for 3 hour in order to convert COOH and OH to the corresponding trimethylsilyl (TMS) esters and ethers. After the reaction, 140 µL internal standard (C_{13} *n*-alkane, 1.43 ng μL^{-1}) was added to the derivatives before injection into gas chromatography/mass spectrometry (GC/MS).

2.3 Gas chromatography/mass spectrometry

Two organic species (i.e. sugars and SOA tracers) were determined on an Agilent model 7890 GC coupled to an Agilent model 5975C mass-selective detector (MSD). The GC instrument was equipped with a split/splitless injector and a DB-5ms fused silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) with the GC oven temperature programmed from 50°C (2 min) to 120°C at 15°C min^{-1}, and then to 300°C at 5°C min^{-1} with final isotherm hold at 300°C for 16 min. Helium was used as carrier gas. The GC injector temperature was maintained at 280°C. The mass spectrometer was operated in the Electron Ionization (EI) mode at 70 eV and scanned in the *m/z* range of 50 to 650 Da. Data were processed using ChemStation software. Each compound was determined through comparing mass spectra with those of authentic standards or literature data. GC/MS response factors were obtained with authentic standards or surrogate standards. Recoveries of the standards that were spiked onto pre-combusted quartz filters and measured as the samples (n = 3) were generally better than 80%. A field blank filter was treated as the real samples for quality assurance. The present data were corrected with field blanks but not for recoveries.

2.4 Positive matrix factorization (PMF) analysis

To further investigate the potential sources of marine organic aerosols, the positive matrix factorization (PMF) analysis are used in this study. For this analysis, the measured ambient concentrations less than or equal to the method detection limit (MDL) were replaced by MDL/2 and associated uncertainties were (5/6)*MDL. For the concentrations greater than the MDL, the calculation of uncertainty is based on the following equation:

$$Uncertainty = \sqrt{(error\ fraction{*}concentration)^2 + (0.5 * MDL)^2} \qquad (1)$$

where the error fraction is a user-provided estimation of the analytical uncertainty of the measured concentration or flux. In the present study, the error fraction was set as 0.2 for all species for receptor-oriented source apportionment analyses (Han et al., 2017).

3 Results and discussion

Concentrations of sugars and biogenic SOA tracers in marine aerosols over the ECS were presented in Table 1. Total abundance of the quantified sugar compounds ranged from 1.8–950 ng m^{-3} with an average of 81.5 ng m^{-3} much lower than those in urban atmosphere in China (Wang et al., 2006), and the nighttime aerosols contained more sugars (average 90.1 ng m^{-3}) than the daytime ones (72.6 ng m^{-3}). Individual sugar compounds also showed higher nighttime concentrations, but still lower than those in urban aerosols (Wang et al., 2011). The total biogenic SOA tracers were in the range of 1.1–135 ng m^{-3} (average 22.9 ng m^{-3}) with lower nighttime abundance (22.2 ng m^{-3}) than daytime (23.6 ng m^{-3}). In contrast to monoterpene and sesquiterpene SOA tracers, the isoprene SOA tracers presented higher levels in the nighttime aerosols (9.6 ng m^{-3}) than those in the daytime samples (7.1 ng m^{-3}).

Generally, higher values of these organics were observed in coastal regions compared with those far away from mainland (Fig. 2, Fig. 4 and Fig. S1), similar to the spatial pattern of lipids, PAHs and phthalates in our previous report (Kang et al., 2017), suggesting the impact from the outflow of continental OM on the basis of back trajectory analysis (Fig. S2-S6).

3.1 Sugars and sugar-alcohols

Sugars, a major class of water-soluble organic constituents in the atmosphere, have been reported to be ubiquitous in marine aerosols (Simoneit et al., 2004b; Burshtein et al., 2011; Fu et al., 2011; Chen et al., 2013). Most of them can serve as tracers of biological primary aerosol particles and biomass burning (Simoneit, 2002; Bauer et al., 2008). Eleven sugar compounds including anhydrosugars (levoglucosan, galactosan, mannosan), sugars (fructose, glucose, sucrose and trehalose) and sugar alcohols (erythritol, arabitol, mannitol and inositol) were measured in marine aerosols collected over the ECS. The concentrations of sugars are shown in Table 1 and Fig. 2. Glucose (0.31–209 ng m^{-3}, mean 18.8 ng m^{-3}) and mannitol (0.03–169 ng m^{-3}, 16.3 ng m^{-3}) were the dominant species, followed by sucrose (0.09–216 ng m^{-3}, 11.7 ng m^{-3}), trehalose (0.08–96.0 ng m^{-3}, 9.4 ng m^{-3}), fructose (0.09–106 ng m^{-3}, 9.1 ng m^{-3}), and levoglucosan (0.09–64.3 ng m^{-3}, 7.3 ng m^{-3}) (Fig. 3). Chen et al. (2013) also reported that glucose and mannitol are the major sugar compounds detected in marine aerosols collected at Chichi-Jima Island during spring and summer. Moreover, nighttime concentrations of all sugars were generally higher than the daytime ones.

Figure 2 presents the temporal variations in sugar compounds determined in the marine aerosol samples collected over the ECS. The concentrations of total sugars were characterized by higher levels in the regions close to continent and/or influenced by land air masses, indicating substantial influence of continental outflow compared to marine air over the pelagic ocean.

3.1.1 Anhydrosugars

Levoglucosan, a thermal degradation production of cellulose (Simoneit, 2002) and a specific indicator for biomass burning (Simoneit et al., 1999), can largely modify the chemical composition of atmospheric aerosols on a regional to global scale. Due to its water solubility, levoglucosan contribute to water-soluble organic carbon in aerosols, significantly enhancing the hygroscopic properties of atmospheric aerosols (Mochida and Kawamura, 2004). The abundance of levoglucosan detected in the present study (0.09–41.2 ng m^{-3}, mean 6.1 ng m^{-3}

and 0.10–64.3 ng m^{-3}, mean 8.4 ng m^{-3} for day and night, respectively) was not the highest among measured sugar species (Fig. 3 and Table 1). The average concentration of levoglucosan is close to those reported at Gosan, Jeju Island in summer (mean 8.0 ng m^{-3}) (Fu et al., 2012). During the whole sampling period, higher concentrations of levoglucosan were found in the samples under the effect of continental air masses based on five-day backward trajectories (Fig. S2-S6), consistent with our previous report about lipids, PAHs and phthalates (Kang et al., 2017). Mannosan and galactosan, isomers of levoglucosan, are produced by pyrolysis of cellulose and hemicellulose and can also act as biomass burning tracers (Simoneit, 2002; Fabbri et al., 2009). Mannosan and galactosan were detected in the samples with similar variation trends to levoglucosan (Table 1 and Fig. 2), further indicating the strong impact of continental biomass burning activities on the marine atmosphere. As shown in Table 1 and Fig. 3, the nighttime average concentrations of all three anhydrosugars were higher than the daytime ones, probably attributable to enhanced biomass combustion and lower height of planetary boundary layer (PBL) as well as the land breeze during the night.

In addition, hard wood tend to contain higher levels of cellulose than hemicellulose, therefore the mass concentration ratios of levoglucosan to mannosan (L/M) can be utilized as a diagnostic parameter for diverse biomass burning substrates (Zhu et al., 2015). Previous studies found that L/M ratios from softwood are in a range of 3–10 and those from hardwood are 15–25, while the ratios from crop residues are even higher (25–40) (Zhu et al., 2015). In this study, the L/M ratios range from 0.71–32 with an average of 4.2, and higher values were observed in the terrestrially influenced aerosols, especially coastal areas near Fujian province (Fig. S7). The lower L/M ratios in our study (average 4.2) suggest that the aerosols were mainly associated with the burning of softwood, consistent with the lower L/M ratios (2.1–4.8) observed on Okinawa Island in May–June (Zhu et al., 2015) and Mt. Fuji (4.6–7.6, mean 5.5) (Fu et al., 2014). It is worth noting that a couple of samples near Fujian Province in Southeast China were characterized by a higher L/M ratio (>20) (Fig. S7), agreeing well with the values of straw burning smokes (Chen et al., 2013). Zhu et al. (2015) also reported combustion of agricultural residues, peat and wood could contribute to high L/M ratios. Therefore, these higher values probably indicate emissions from terrestrial burning of straw residues, which could affect the chemical components of aerosols in the western North Pacific via long-range atmospheric transport as confirmed by backward trajectories (Fig. S5).

3.1.2 Sugar alcohols

Sugar alcohols detected in these samples consist of arabitol, mannitol, inositol and erythritol, which had similar temporal patterns (Fig. 2e-h). Higher abundances of sugar alcohols observed in the terrestrially influenced aerosol samples suggesting a significant contribution from terrestrial source (Fig. S2-S6). While the marine fungi and algae, which can also release fungal spores into the marine atmosphere via bubble bursting, contribute little to the sugar alcohols in the coastal aerosols. Obviously, mannitol and arabitol were the most abundant sugar alcohols detected in the present study (Fig. 3 and Table 1), ranging from 0.03–169 ng m^{-3} (16.3 ng m^{-3}) and 0.02–51.0 ng m^{-3} (5.1 ng m^{-3}), respectively. A strong positive correlation between arabitol and mannitol were found in marine aerosols ($p < 0.001$, $r = 0.996$, N = 51), suggesting a similar origin. Mannitol and arabitol are very common in fungi, and are the most frequently occurring sugar alcohols in plants (Burshtein et al., 2011), which can be utilized to assess the contribution of fungal spores to the aerosol OC (Bauer et al., 2008). For instance, mannitol is particularly abundant in algae (Burshtein et al., 2011). The peak concentrations of sugar alcohols were found in the nighttime samples, which can be attributed to the increased activities of yeasts and fungi at night (Graham et al., 2003). Moreover, the maxima concentrations of these sugar polyols, especially arabitol and mannitol, were observed in offshore regions in early summer (June) (Fig. 2e-h), likely due to the more active microbial activities resulting from warmer temperature in June and more biota in coastal regions (Fig. 1).

3.1.3 Sugars

Glucose, fructose, sucrose, and trehalose are the primary saccharides measured in marine aerosols over the ECS. Glucose was the dominant sugar compound (0.31–209 ng m^{-3}, 18.8 ng m^{-3}), followed by sucrose (0.09–216 ng m^{-3}, 11.7 ng m^{-3}) (Fig. 2i-l and Fig. 3). Glucose and fructose originate from plant materials, such as pollen, fruits and their fragments (Graham et al., 2003; Fu et al., 2012). Both glucose and fructose presented higher levels in the coastal areas, demonstrating great contribution from terrestrial vegetation. Medeiros and Simoneit (2007) reported that high abundance of glucose associated with lower molecular weight fatty acids (mainly C_{16}) was attributed to the spring bloom of algae. In our study, $C_{16:0}$ fatty acid correlated well with glucose ($p = 0.001$, $r = 0.46$, N = 51), which suggests that marine sources also contributed to the particulate glucose in the oceanic atmosphere. It was noted that fructose was obviously related to glucose ($p < 0.001$, $r = 0.94$, N = 51), indicating they share similar sources. Sucrose, as a predominant sugar species in the phloem of plants as well as developing flower buds, is reported to be the richest and dominant component of airborne pollen grains (Graham et al., 2003). High abundance of sucrose along with fructose and glucose observed in our study implies a large emission of airborne pollen grains into the marine atmosphere over the ECS. Significantly, the concentration of glucose, fructose and sucrose were highest at the beginning of June in early summer (Fig. 2i-l), probably attributable to an enhanced pollen emission, because pollen counts tend to be highest in late spring/early summer in temperate zones (Graham et al., 2003). Such peak concentrations in early June are in accord with a previous study by Pashynska et al. (2002). Trehalose, a fungal metabolite, is present in a variety of microorganisms (fungi, bacteria, yeast and algae), and a few higher plants as well as invertebrates (Medeiros et al., 2006a). Thus, trehalose can be used as a microbial biomarker and stress protectant. Furthermore, trehalose was reported to be the most abundant sugar in soil (Medeiros et al., 2006b; Rogge et al., 2007; Jia and Fraser, 2011), thus the enrichment of trehalose in aerosols can be indicative of soil resuspension and unpaved road dust (Simoneit et al., 2004a; Fu et al., 2012). The trehalose in our study was positively correlated with non-sea-salt calcium (nss-Ca^{2+}) ($p < 0.01$, $r = 0.43$, N = 51), the best tracer for soil dust (Virkkula et al., 2006), suggesting the atmospheric trehalose over the ECS was mainly derived from resuspension of soil particles. Higher abundance of trehalose in coastal regions (Fig. 2l), may be in connection with the outflow of Asian dust primarily occurring in winter/spring (Fu et al., 2012), and inland soil resuspension/dust aerosols.

3.2 Secondary organic aerosols

The sum of all SOA tracers ranged from 1.1–135 ng m^{-3} (22.9 ng m^{-3}), which were higher than previous report of marine aerosols (0.19–27 ng m^{-3}, 6.6 ng m^{-3}) (Fu et al., 2011), but much lower than those in the continental sites (Fu et al., 2010; Ding et al., 2014). These differences suggest that the major source of SOA tracers over the ECS is probably of terrestrial origin. Specifically, the total concentrations of detected isoprene SOA-tracers ranges from 0.15–64.0 ng m^{-3} (8.4 ng m^{-3}), comparable to those reported in marine aerosols (mean 8.5 ng m^{-3}) (Hu et al., 2013), but lower than those of urban aerosols (Ding et al., 2014; Ren et al., 2017); total monoterpene SOA-tracers in the range of 0.26–87.2 ng m^{-3} (11.6 ng m^{-3}) lower than those in urban aerosols as well (Ren et al., 2017); total sesquiterpene SOA-tracers ranged between 0.16 and 17.2 ng m^{-3} (2.9 ng m^{-3}). Such phenomena that BSOA derived from monoterpenes are more abundant than those from isoprene were also reported in

Chinese urban areas (Ren et al., 2017). On the whole, biogenic SOA tracers exhibited higher loadings in the coastal areas than those remote sampling sites, further indicating that long-range atmospheric transport of terrestrial aerosols has significant influence on the chemical composition and abundance of SOA over oceans. Marine VOC spatial distributions are expected to be linked to the distributions of photosynthetic pigments in seawater, such as chlorophyll-a (Ooki et al., 2015). The higher concentrations of chlorophyll-a in the coastal regions (Fig. 1) stand for higher biological activities and more emission of VOCs, which agree well with higher SOA tracers over the coastal waters. Such spatial variations in biogenic SOA tracers are in agreement with a previous report about marine organic aerosols collected during a round-the-world cruise (Fu et al., 2011).

3.2.1 Isoprene SOA tracers

Isoprene is a reactive biogenic hydrocarbon and primarily originates from terrestrial photosynthetic vegetation (e.g. trees and plants). Marine phytoplankton and seaweed can also emit isoprene (Yokouchi et al., 1999; Shaw et al., 2010). Moreover, bacteria produce isoprene as well, and the bacterial isoprene production is temperature-dependent (Kurihara et al., 2010). In spite of much lower emission strength in the ocean region, more recent researches have suggested that the oceanic source of isoprene significantly impact atmospheric chemistry and cloud microphysical properties in the remote marine boundary layer because of its high reactivity (about 1–2 hour lifetime) (Hackenberg et al., 2017).

Six isoprene SOA tracers, including 2-methylglyceric acid, three C_5-alkene triols, and two 2-methyltetrols (2-methylthreitol and 2-methylerythritol), were identified in the marine aerosols over ECS. Isoprene SOA tracers showed diurnal variations with higher average concentrations at night (Fig. 4a-c, Fig. 5, Fig. S8), consistent with the report by Fu et al. (2010). The higher abundance during the night can be explained by the enhanced gas-to-particle partition at cooler temperatures during the nighttime and/or increased input of continent-originated isoprene-SOA into the oceanic atmosphere via land-sea breeze circulations at night. However, T-test showed that the difference between daytime and nighttime concentrations for 2-methyltetrols, C_5−alkene triols and 2-MGA was not that significant ($p > 0.05$). As expected, much higher concentrations of isoprene tracers were observed in coastal regions, where continental outflows exert larger effects from spring to early summer. For the remote ocean, terrestrial sources have weak impacts because of the short atmospheric lifetime of isoprene and the dilution effects during long-range atmospheric transport. In addition to the effect of continental outflow, more nutrients in the coastal and estuarine regions could be another factor responsible for the higher levels of isoprene SOA tracers compared to the pelagic areas. Because nutrient-rich surface water can promote the development of phytoplankton blooms and increases chlorophyll-a concentrations. Chlorophyll-a is a measure of phytoplankton, or algal, biomass (Quinn et al., 2014) and currently most widely used proxy for predicting isoprene concentrations in water (Hackenberg et al., 2017). Numerous studies reported the positive relationship between isoprene emission and chlorophyll-a in the surface seawater (Zhu et al., 2016; Hackenberg et al., 2017). In the present study, the temporal and spatial distributions of chlorophyll-a at the ECS surface during the whole sampling period are characterized by higher coastal levels, such as waters near Zhejiang and Fujian provinces, but lower abundance in eastern Taiwan and the remote sea (Fig. 1). Thus, high chlorophyll-a waters in coastal locations mean more isoprene emissions than remote open waters. However, the isoprene in the remote ocean may mainly originate in situ from biological production by marine biota at the ocean surface.

The low-NO_x products 2-methyltetrols with mass concentrations ranging from 0.03–41.9 ng m^{-3} (4.8 ng m^{-3}) were the major species among the isoprene SOA tracers, in line with early report about summer aerosols in China (Ding et al., 2014). Specially, concentration ranges of 2-methyltetrols were 0.11–17.0 ng m^{-3} (3.8 ng m^{-3}) during the daytime and 0.03–41.9 ng m^{-3} (5.7 ng m^{-3}) at night with 2-methylerythritol being about 2.1-fold more abundant than 2-methylthreitol. This ratio is similar to those calculated in previous studies (Ion et al., 2005; Cahill et al., 2006; Fu et al., 2010). The atmospheric levels of 2-methyltetrols are comparable to those reported in marine aerosols collected during a round-the-world cruise (0.07–15 ng m^{-3}, 2.4 ng m^{-3}) (Fu et al., 2011). However, these values are small compared to those from terrestrial emissions, such as mountain (Cahill et al., 2006; Fu et al., 2014) and forest aerosols (Claeys et al., 2004a; Fu et al., 2010; Miyazaki et al., 2012). A significant positive relationship between 2-methyltetrols and levoglucosan ($p < 0.001$, $r = 0.87$, N = 51) in our study suggests that biomass burning may also generate the precursors of 2-methyltetrols followed by photochemical reactions (Xie et al., 2014). Besides, 2-methyltetrols correlated with C_{29} *n*-alkane (the dominant species of terrestrial higher plant waxes) as well ($p < 0.001$, $r = 0.74$, N = 51), suggesting these organic tracers originate from higher plants or from similar source regions as well. The correlations above illustrate that terrestrial emissions (e.g. biomass burning and higher plants) contributed significantly to the levels of 2-methyltetrols in the marine atmosphere.

C_5-Alkene triols are formed from photooxidation of isoprene under low-NO_x conditions (Surratt et al., 2006; Lin et al., 2013). They were detected in all the samples ranging from (0.03–14.6 ng m^{-3}, 2.2 ng m^{-3}), which are higher than those reported in Arctic aerosols (0.01–0.15 ng m^{-3}) (Fu et al., 2009) and other marine aerosols (0.002–4.6 ng m^{-3}, 0.65 ng m^{-3}) (Fu et al., 2011); but lower than the atmospheric levels of mountain aerosols (Fu et al., 2010; Fu et al., 2014) and subtropical urban aerosols from Hong Kong (Hu et al., 2008). Such a difference illustrates the outflow of continental aerosols, which can be confirmed by the significant positive correlations between C_5-alkene triols and tracers of terrestrial emissions, such as C_{29} *n*-alkanes ($p < 0.001$, $r = 0.78$, N = 51) and levoglucosan ($p < 0.001$, $r = 0.87$, N = 51). It was found that 2-methyltetrols correlated well with C_5−alkene triols in marine aerosols over ECS ($p < 0.001$, $r = 0.86$, N = 51), suggesting a similar formation mechanism or common sources. However, the mass concentration ratios of C_5-alkene triols to 2-methyltetrols showed significant variation in different sampling sites (Fig. 6a), indicating different formation pathways, consistent with a previous report (Fu et al., 2010).

Concentrations of 2-methylglyceric acid (2-MGA), formed by photooxidation of isoprene under high-NO_x ($NO_x = NO + NO_2$) conditions (Surratt et al., 2006), were in the range of 0.09–8.3 ng m^{-3} (1.4 ng m^{-3}) being greatly lower than those in mountain aerosols (Cahill et al., 2006; Fu et al., 2010; Fu et al., 2014), implying much stronger influence of NOx on isoprene SOA formation in continental aerosols. 2-MGA is a possible further oxidation product of methacrolein and methacrylic acid, which are two major gas-phase oxidation products of isoprene (Claeys et al., 2004b; Edney et al., 2005; Fu et al., 2009). 2-MGA was related to C_{29} *n*-alkanes ($p < 0.001$, $r = 0.84$, N = 51) and levoglucosan ($p < 0.001$, $r = 0.81$, N = 51) as well, again suggesting a terrestrial input. These isoprene-SOA tracers in marine aerosols over the ECS may stem from terrestrial higher plants and biomass burning, and then were oxidized during the transport to the oceanic atmosphere. Similar correlations between isoprene-derived SOA tracers and levoglucosan were mentioned in previous study, which reported that biomass burning enhanced the isoprene-SOA formation (Li et al., 2018). Additionally, 2-methyltetrols are higher generation products than 2-MGA (Fu et al., 2014), but the ratios of 2-MGA to 2-methyltetrols did not vary significantly with cruise track. However, a couple of high ratios were observed in the ocean-air influenced aerosols, suggesting the importance of marine source for fresh isoprene-derived SOAs in the atmosphere (Fig. 6b).

NO_3^- was found to be related to 2-MGA, 2-methyltetrols and C_5-alkene triols ($p < 0.001$, $r = 0.60$–0.71, N = 51). The ratio of 2-MGA to 2-methyltetrols was found to be negatively correlated with particulate NO_3^- ($p < 0.05$, $r = -0.31$, N = 51). These relationships reveal that there may be a close connection between formation of isoprene SOA and NO_3^- in the marine boundary layer.

3.2.2 Monoterpene SOA tracers

The detected α/β-pinene oxidation products in the study consist of pinonic, pinic acids, 3-hydroxyglutaric acid (3-HGA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). They are derived from the photooxidation of α/β-pinene with O_3 and OH radicals (Hoffmann et al., 1997; Yu et al., 1999; Glasius et al., 2000; Iinuma et al., 2004). Since monoterpenes account for around 35% of the global biogenic VOCs' emissions, these compounds have been utilized to estimate the role of monoterpene oxidation in the SOA formation (Griffin et al., 1999). Monoterpenes were chiefly emitted from needle leaf trees. In this study, monoterpene-SOA tracers were found to be positively correlated to levoglucosan with $p < 0.001$ (r ranges from 0.68–0.82), indicating terrestrial biomass burning made substantial contributions to the formation of monoterpenes, then being transported to the oceanic atmosphere. Generally, total monoterpene-SOA tracers in our study showed a major peak in spring (Fig. S1g), in agreement with a previous study (Zhu et al., 2016). Pinonic and pinic acids, well-known tracers for α/β-pinene, ranged from (0.02–1.6 ng m^{-3}, 0.47 ng m^{-3}) and (0.16–14.9 ng m^{-3}, 3.4 ng m^{-3}), respectively (Table 1). Their concentrations were higher than those in high Arctic aerosols (average 69 pg m^{-3} and 514 pg m^{-3}, respectively) (Fu et al., 2009). In addition, concentrations of pinic acid were 7 times higher than pinonic acid, similar to an earlier report (Fu et al., 2009). The vapour pressure of pinic acid is about 2 orders of magnitude lower than pinonic acid (Bhat and Fraser, 2007). Thus, pinic acid can saturate and readily nucleate, being expected to have a higher fraction in the aerosol phase than pinonic acid.

Two novel monoterpene SOA tracers, 3-hydroxyglutaric acid (3-HGA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), were also detected in these marine aerosols. Both of them are reported to be higher-generation products of α-pinene photooxidation (Szmigielski et al., 2007; Kourtchev et al., 2009). The concentration ranges of 3-HGA in marine aerosols over ECS were lower than those of aerosols in Mt. Tai, central east China (Fu et al., 2010), but comparable to other studies about marine aerosols (Fu et al., 2011). The average abundance of atmospheric MBTCA for all samples were 5.6 ng m^{-3} with mean concentrations of 6.8 ng m^{-3} and 4.5 ng m^{-3} during the day and night, respectively, more abundant than 3-HGA (2.2 ng m^{-3}). Interestingly, these mean values of MBTCA were comparable to those of mountain aerosols (Fu et al., 2010), but still higher than the marine aerosols collected on the remote seas (Fu et al., 2011). Since the ECS is adjacent to Mainland China, the atmospheric boundary layer in these regions would inevitably be affected by continent-derived air masses, as supported by the spatial pattern of individual SOA tracers (Fig. 4 and Fig. S1), in particular of the peaks occurring in the coastal areas. Furthermore, in contrast to isoprene SOA tracers, monoterpene SOA tracers commonly exhibit higher average daytime concentrations (Table 1 and Fig. 5), but T-test showed no significant difference ($p > 0.05$) between daytime and nighttime concentrations for both total and individual monoterpene SOA tracers. The concentration ratio of 3-HGA plus MBTCA to pinic acid ((3HGA+MBTCA)/pinic) showed higher values in the terrestrially influenced aerosols (Fig. 6c). Besides, this mass concentration ratios were basically higher during the daytime (mean 2.0) than nighttime (1.9), indicating that aged aerosols are more abundant in the daytime.

3.2.3 Sesquiterpene SOA tracers

The analysis of sesquiterpenes is a great challenge due to their high reactivity and relatively low vapour pressure. However, the aging of β-caryophyllene derived SOA has proved its significant effects on all CNN-relevant properties (Asa-Awuku et al., 2009). β-caryophyllinic acid is one of the most abundant species among sesquiterpenes originating from plants (Duhl et al., 2008). It is an ozonolysis or photooxidation product of β-caryophyllene (Jaoui et al., 2007). Moreover, sesquiterpenes accumulated in leaves and woods can be emitted during biomass combustion (Ciccioli et al., 2014).

The atmospheric levels of β-caryophyllinic acid were 0.16–17.2 ng m^{-3} (mean 2.9 ng m^{-3}), with 0.17–17.2 ng m^{-3} (3.5 ng m^{-3}) during daytime and 0.16–9.6 ng m^{-3} (2.3 ng m^{-3}) during nighttime, respectively (Table 1). As expected, β-caryophyllinic acid correlated well with levoglucosan ($p < 0.001$, $r = 0.61$, N = 51) in agreement with earlier report (Ding et al., 2016), indicating substantial contribution of terrestrial biomass burning to sesquiterpenes' loading in the marine atmosphere. On the other hand, biomass-burning processes (e.g. crop straw combustion and forest fires) can raise ambient and/or leaf temperature to some extent, consequently probably enhancing the emission of sesquiterpenes from trees and plants.

Many researches have proved that sesquiterpene emissions increase significantly with increasing ambient temperatures (Tarvainen et al., 2005; Jaoui et al., 2007). Ambient temperature seems to be the dominant factor controlling temporal variation in sesquiterpene emission although other factors contribute (Duhl et al., 2008). An early study reported that emission rates of sesquiterpene were 1.2–3 times higher in the daytime as well (Duhl et al., 2008). All the reports described above perfectly interpret much higher concentrations of β-caryophyllinic acid during daytime in our study. The abundance of β-caryophyllinic acid in this study are higher than those reported in the remote marine aerosols during a round-the-world cruise, but comparable to the maximum concentration of 2.5 ng m^{-3} observed at California coast (Fu et al., 2011); however, the concentrations of β-caryophyllinic acid were much lower than those of Mt. Tai aerosols, central east China (average 12 ng m^{-3} for both daytime and nighttime aerosols) (Fu et al., 2010). The spatial distributions of β-caryophyllinic acid also presented higher levels in coastal regions than other sampling sites (Fig. 4h), again proving contribution of terrestrial aerosols.

3.3 Contributions of biogenic primary and secondary sources

To assess the relative abundances of organic aerosols from primary and secondary emission sources, tracer-based methods are employed to evaluate their contributions to the marine ambient OC. For example, mannitol and arabitol determined in marine aerosols were used to calculate the contributions of fungal spores to OC (Bauer et al., 2008); the average mass percent ratios of levoglucosan to OC (8.14%) are used to investigate the biomass burning derived OC (Fu et al., 2014). Besides, biogenic SOA tracers detected in the present study are utilized to evaluate the SOC formation resulting from the oxidation of isoprene, α-pinene and β-caryophyllene through a tracer-based method reported by Kleindienst et al. (2007). This method used the laboratory-derived mass fractions (f_{soc}) of marker species generated from known precursors into SOC concentrations. Specifically, the f_{soc} values used in our study is 0.155±0.039 for isoprene, 0.231±0.111 for α-pinene and 0.023±0.005 for β-caryophyllene, respectively (Kleindienst et al., 2007). Through dividing the sum of tracer compounds measured in these marine samples by f_{soc}, an estimate of the contribution of each SOA to the total marine SOC concentration was determined and the results were presented in Table 2.

Biomass burning derived OC in the whole samples is in the range of 1.1–790 ngC m^{-3} (89.6 ngC m^{-3}), with higher levels in the nighttime (1.3–790 ngC m^{-3}, 103 ngC m^{-3}) compared to those (1.1–506 ngC m^{-3}, 75.5 ngC m^{-3}) in the daytime. Higher concentrations of biomass-burning OC near the Asian continent than those over the remote oceans (Fig. 7) suggest that continental biomass-burning tracers were possibly removed by dry and/or wet deposition of airborne particles, photodegradation by free radicals in the atmosphere or other atmospheric dilution mechanism during long-range transport to the western North Pacific. Fungal-spore-derived OC for all samples ranged from 1.2–1840 ngC m^{-3} (180 ngC m^{-3}), accounting for 0.03–19.8% (3.1%) of OC, higher than those of biomass-burning-derived OC (Table 2). The nighttime fungal-spore-derived OC (1.2–1840 ngC m^{-3}, 203 ngC m^{-3}) is higher than those of daytime ones (1.3–911 ngC m^{-3}, 157 ngC m^{-3}), possibly associated with intensified activities of yeasts and fungi during nighttime (Fu et al., 2012). As we all known, evenings tend to have higher moist content, which exerts a stronger influence on microbial activity than temperature (Liang et al., 2003). Similar higher levels of fungal-spore-derived OC were also observed in the aerosols collected in coastline waters, probably due to more intensified microbial activities in the coastal regions as discussed previously. β-caryophyllene SOC (6.9–747 ngC m^{-3}, 126 ngC m^{-3}, with 7.4–747 ngC m^{-3}, mean 153 ngC m^{-3} during the day and 6.9–416 ngC m^{-3}, mean 100 ngC m^{-3} at night) is found to be dominant contributor among the measured biogenic SOCs over the ECS (the average concentrations were 39.8 ngC m^{-3} and 50.2 ngC m^{-3} for isoprene SOC and α/β-pinene SOC, respectively). Moreover, β-caryophyllene SOC account for 0.36–5.3% (2.4%) of OC, about 2–3 times as high as those of isoprene (0.13–3.8%, 0.83%) and monoterpene SOC (0.08–3.5%, 0.98%). Therefore, an emission inventory for sesquiterpenes in marine aerosols over the ECS will be helpful for further understanding formation of biogenic SOA in this region. Zhu et al. (2016) also reported that the sesquiterpene-derived SOC was more abundant than isoprene- and monoterpene-derived SOC for the aerosols collected in Okinawa, Japan.

The higher levels of sesquiterpene-SOC than monoterpene- and isoprene-SOC may be due to the differences in the gas/particle partitioning of oxidation products from different VOCs, given that longer chain sesquiterpenes ($C_{15}H_{24}$) have more carbon atoms than monoterpenes ($C_{10}H_{16}$) and isoprene (C_5H_8), decreasing the vapour pressures of their oxidation products (Fu et al., 2016). The levels of SOCs stemmed from isoprene, monoterpenes and sesquiterpene in the marine aerosols over the ECS were much lower than those of $PM_{2.5}$ samples in Hong Kong, China during summer (Hu et al., 2008) and those observed in Mt. Tai aerosols (Fu et al., 2010). The sum of biogenic SOCs over the ECS is 11.3–1060 ngC m^{-3} (216 ngC m^{-3}), much lower than that of Mt. Fuji aerosols (227–1120 ngC m^{-3}, 542 ngC m^{-3}) (Fu et al., 2014) and those in the Mt. Tai aerosols (420–3100 ngC m^{-3}) (Fu et al., 2010), but higher than those observed in marine aerosols collected during a round-the-world cruise covering most remote oceans (Fu et al., 2011) and those reported in the Arctic aerosols (average 14.6 ngC m^{-3}) (Fu et al., 2009). Such difference between terrestrial aerosols and marine aerosols highlights the outflow of continental aerosols again. In terms of spatial distributions, biogenic SOCs calculated from these compounds showed higher loadings in the locations close to the coastline or significantly influenced by terrestrial air (Fig. 8a-b), also validating strong influence of continental origin. Generally, the total concentrations of biogenic SOC (216 ngC m^{-3}) are higher than those of biomass-burning-derived OC (89.6 ngC m^{-3}) and fungal-spore-derived OC (180 ngC m^{-3}) (Table 2), presenting greater contribution from biogenic SOA to the marine aerosols, in agreement with the report by Fu et al. (2014).

In order to compare the relative contribution of marine and continental sources to total OC in the oceanic atmosphere, the whole sampling area was divided into five regions from south to north according to the spatial distribution of aerosol samples, i.e. northern waters of ECS, nearby waters in the ECS, seas adjacent to Fujian and Zhejiang provinces, eastern waters of Taiwan. Five-day HYSPLIT back trajectory analysis showed that the atmosphere over waters north of ECS were mainly controlled by marine air masses, while aerosol samples achieved on June 12 showed great influence from South Korea and North China as well (Fig. S2). Aerosol samples in waters of ECS were basically under the control of marine air masses, except for the samples collected on May 20, which were also affected by terrestrial air from the Asian mainland (Fig. S3).

In general, aerosols collected off the eastern coast of Taiwan Island were affected by air masses from the remote sea, but some aerosols collected on May 22–23 were also influenced by air masses coming from Southeast Asia (Fig. S4). In contrast, air masses from Asian mainland had substantial impacts on the samples collected near Fujian and Zhejiang province (Fig. S5-S6). On the whole, the aerosols strongly affected by terrestrial sources (e.g. Asian mainland, Southeast Asia and South Korea) tend to own higher levels of sugars and SOA tracers (Fig. 2 and Fig. 4). The contributions of biomass-burning-derived OC, fungal-spore-derived OC, and biogenic SOCs to OC (%) in these five sampling regions were presented in Fig. 9. Generally, the average contributions of biogenic SOCs, biomass-burning OC and fungal-spore OC to OC near Zhejiang and Fujian waters were higher than the other sampling areas, especially for the fungal-spores-OC (7.5±6.8 for Zhejiang waters, 4.0±2.8 for Fujian waters, 2.6±3.2 for the northern waters of ECS, 1.9±1.7 for eastern waters of Taiwan, and 1.5±1.4 for ECS, respectively) and biomass-burning-OC (2.8±2.6 for Zhejiang waters, 2.7±1.8 for Fujian waters, 1.3±0.92 for the northern waters of ECS, 0.52±0.36 for eastern waters of Taiwan, and 0.96±1.7 for ECS, respectively). Such spatial variations were closely associated with different contributions of land and marine sources to the oceanic atmosphere.

Figures S2-S6 display a strong influence from land air masses in waters around Zhejiang and Fujian provinces, while the atmosphere over northern waters of ECS, ECS and eastern waters of Taiwan Island basically came under the influence of relatively clean marine air. Interestingly, the average percentage of isoprene SOC in the eastern waters of Taiwan was slightly larger compared to other regions. In light of back trajectory analysis, aerosols in this region were mainly affected by terrestrial photosynthetic vegetation (e.g. trees and plants) in Southeast Asia and/or marine biota (e.g. phytoplankton, seaweed and bacteria) (Fig. S4). Sesquiterpene-derived SOC was found to be the most abundant SOC species in all five areas (2.9±0.87 for Zhejiang waters, 3.1±1.7 for Fujian waters, 2.1±0.80 for the northern waters of ECS, 2.2±1.2 for eastern waters of Taiwan, and 2.2±1.3 for ECS, respectively) in comparison with other SOCs derived from isoprene and monoterpene. On the other hand, the nighttime contributions of biomass-burning OC, fungal-spores OC and biogenic SOCs to OC were commonly greater than the daytime ones in all five regions (Fig. S9). For instance, the contributions of biomass-burning-OC and fungal-spores-OC to OC during nighttime in the seas near Zhejiang (3.9±3.5 and 9.3±8.0, respectively) are significantly greater than those in the daytime (1.9±1.2 and 6.0±6.3, respectively). Such enhanced contributions in the evening were likely to be in connection with intensified emissions, decreased height of PBL and land-sea breeze circulations. The downward movement of PBL does not facilitate dispersion of pollutants and lead to increases in aerosol concentration in the lower PBL (Li et al., 2017). The prevailing land breeze in the nighttime in coastal areas could bring plentiful terrestrial particles to the clean marine atmosphere. Such difference between daytime and nighttime contributions illustrates that land-sea breeze circulation and PBL can be another important factor influencing organics in marine aerosols.

3.4 Source apportionment by PMF

3.4.1 Analysis of source profiles

After testing runs with different number of factors (5–9), eight factors were chosen on basis of the minimum value of Q (goodness of fit parameters) and probable source profile expected from the study region.

Figure 10 illustrates the first source had high loadings of Na^+ (90.8%), suggesting a contribution from sea salt. This profile also contained a significant amount of SO_4^{2-}, which can react with sea-salt particles and release HCl gas, leaving lower Cl^-/Na^+ ratio (0.1) than that of sea water (1.8) (Boreddy et al., 2014).

The second source shows high loadings of levoglucosan (66.3%), arabitol (55.0%), mannitol (51.1%) and trehalose (50.4%), representing mixed sources of biomass burning and fungal spores (Simoneit et al., 1999; Medeiros et al., 2006a; Bauer et al., 2008). Yang et al. (2012) found an enhanced abundance of fungal tracers on account of biomass burning activities, during which large numbers of fungi could be dispersed into the surrounding atmosphere or be carried upward with the warm plume to other fields via long-distance atmospheric transport.

The third source can be interpreted as crustal dust because of high loadings of Mg^{2+} (66.1%) and Ca^{2+} (64.2%), characteristic elements of soil/crustal dust (Xu et al., 2016). This source may include airborne road dust, construction dust and windblown soil particles, which are derived primarily from terrestrial source. This source also contains large amount of sulfate, which can react with crustal aerosols forming metal sulphates such as $CaSO_4$ and $MgSO_4$.

The fourth factor is characterized by dominance of NH_4^+ (58.4%) and SO_4^{2-} (49.7%), which can be classified as secondary ammonium sulfate. The molar ratio of NH_4^+ and SO_4^{2-} was 2.9 in this profile, suggesting that $(NH_4)_2SO_4$ was the dominated sulfate form in the marine atmosphere over the ECS. Due to its long lifetime in the atmosphere, terrestrial SO_4^{2-} could be transported long distance to coastal areas and even to the remote sea (Itahashi et al., 2017), affecting chemical composition of oceanic atmosphere.

The fifth factor exhibits high loadings of di-isobutyl (DiBP) and di-n-butyl (DnBP), dominant species of phthalates in the marine aerosols over the ECS, which is assigned to plastic materials' emission likely from industry, agriculture and domestic application in coastal regions.

The sixth factor has high loadings from sucrose (85.3%) followed by fructose (50.9%), implies a significant emission from airborne pollen grains to the marine atmosphere over the ECS during late spring to early summer (Fu et al., 2012).

The seventh profile presents high loading of Cl, likely to be associated with coal combustion, which provides significant releases of chlorine (McCulloch et al., 1999; Sun et al., 2013). Another confirmation is high concentration of SO_4^{2-} from this profile, since coal consumption can produce mass sulfate as well.

The eighth factor illustrates high loadings of NO_3^- (67.5%) and biogenic SOA tracers, especially the monoterpene SOA tracers, i.e. PA (67.5%) and MBTCA (65.2%). This factor could be attributed to the photochemical oxidation products stemmed from emission of vehicle and biogenic VOCs. Formation of secondary nitrate depends on NO_x, which is mainly produced from power plants and mobile sources (Kim et al., 2006; Heo et al., 2009). Anthropogenic NO_x could also enhance biogenic SOA formation via nitrate radical oxidation of monoterpenes (Xu et al., 2015). The positive correlations between NO_x and isoprene-derived SOA tracers as discussed before in our study also suggest NO_3^- and BSOA may share common formation pathways. Previous study once pointed out that nitrogen-containing species act a pivotal part in the formation and fate of SOA through varying radical and oxidant regimes and particle properties, such as volatility and hygroscopicity (Chen et al., 2017), agreeing well with our results.

Overall, the eight sources based on PMF were sea salt, biomass burning and fungal spores, crustal dust, secondary sulfate ammonia, plastic emission, pollen grains, coal combustion, and secondary nitrate and BSOA, which contributed to the TSP over the ECS of 16.9%, 3.5%, 8.0%, 28.5%, 6.3%, 2.0%, 14.3% and 20.4% in average, respectively (Fig. 11). The results of PMF present that secondary origin and marine natural emissions could be the main sources for the aerosols over the ECS.

3.4.2 Temporal and spatial variation in sources

Figure 12 shows the temporal and spatial variation in each profile during the day and the night. The contribution of each source changes over time and varies with distance from the continent. In general, higher levels contributed by biomass burning, fungal spores, crustal dust, pollen grains, coal combustion, secondary nitrate and BSOA, were basically observed in coastal aerosols and/or terrestrially influenced aerosols, suggesting strong influence of continental air from East Asia and Southeast Asia in light of the back trajectories and wind directions during the sampling periods (Fig. S2-S6 and S10). However, the contributions from sea salt, indicative of oceanic emission, tend to be higher in the aerosols mainly affected by marine air masses. Our study demonstrates that primary and secondary OM of terrestrial origin play an important role in the marine aerosol chemistry over the western North Pacific through long-range atmospheric transport in addition to natural emission of ocean.

4 Conclusions

In summary, atmospheric concentration, spatial distribution and source appointment of sugars and biogenic SOA tracers were studied for the coastal and remote marine aerosols. Higher concentrations of sugars and BSOA tracers were observed in the atmosphere around coastal waters and/or in the terrestrially influenced regions in comparison with the remote oceans, suggesting that continent origin contributed a lot to the abundance of sugars and BSOA tracers in the marine atmosphere. Glucose was the dominant sugar species, followed by mannitol among the total identified sugar compounds. Biogenic SOC were characterized by a predominance of β-caryophyllene oxidation products in comparison with isoprene and α/β-pinene tracers. The contributions of biomass-burning-derived OC, fungal-spore-derived OC, and biogenic SOC to OC (%) were greater in the marine aerosols affected by land air masses. The results of PMF present that secondary origin and marine natural emissions may be the main sources for the aerosols over the ECS. Our study demonstrates that both primary and secondary organic aerosols of terrestrial origin have great influences on the marine aerosol chemistry over the western North Pacific through long-range atmospheric transport.

Data availability. The data for this paper are available upon request from the corresponding author (fupingqing@tju.edu.cn).

Competing interests. The authors declare that they have no conflict of interest.

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Table 1. Concentrations (ng m^{-3}) of saccharides and biogenic SOA tracers measured in the marine aerosols collected over the East China Sea during May to June 2014.

Compounds	Whole period (*n* = 51)		Daytime (*n* = 25)		Nighttime (*n* = 26)	
	Mean	Range	Mean	Range	Mean	Range
Anhydrosugars						
Galactosan	0.59	0.02–3.9	0.56	0.04–3.6	0.62	0.02–3.9
Mannosan	1.4	0.06–10.2	1.2	0.08–5.2	1.6	0.06–10.2
Levoglucosan	7.3	0.09–64.3	6.1	0.09–41.2	8.4	0.10–64.3
Sugar Alcohols						
Erythritol	1.3	n.d.[a]–16.9	0.87	0.02–4.60	1.6	n.d.–16.9
Arabitol	5.1	0.02–51.0	4.5	0.06–26.7	5.7	0.02–51.0
Mannitol	16.3	0.03–169	14.1	0.08–81.3	18.4	0.03–169
Inositol	0.57	0.01–7.7	0.47	0.01–2.8	0.67	0.01–7.7
Sugars						
Fructose	9.1	0.09–106	8.1	0.09–56.5	10.2	0.32–106
Glucose	18.8	0.31–209	17.8	0.31–106	19.7	0.47–209
Sucrose	11.7	0.09–216	9.7	0.14–136	13.5	0.09–216
Trehalose	9.4	0.08–96.0	9.1	0.08–60.7	9.7	0.10–96.0
Subtotal	81.5	1.8–950	72.6	1.0–525	90.1	1.8–950
Isoprene SOA tracers						
2-methylthreitol	1.5	0.01–12.7	1.2	0.04–5.2	1.9	0.01-12.7
2-methylerythritol	3.2	0.02–29.1	2.5	0.08–11.8	3.9	0.02–29.1
Sum of 2-methyltetrols	4.8	0.03–41.9	3.8	0.11–17.0	5.7	0.03–41.9
2-Methylglyceric acid (2-MGA)	1.4	0.09–8.3	1.2	0.20–3.6	1.6	0.09–8.33
C_5-Alkene triols [b]	2.2	0.03–14.6	2.1	0.06–14.6	2.3	0.03–13.8
Subtotal	8.4	0.15–64.0	7.1	0.42–35.2	9.6	0.15–64.0
α/β-pinene (monoterpene) SOA tracers						
3-Hydroxyglutaric acid (3-HGA)	2.2	0.03–14.1	2.3	0.08–14.1	2.1	0.03–7.7
Pinonic acid (PNA)	0.47	0.02–1.6	0.49	0.06–1.6	0.46	0.02–1.6
Pinic acid (PA)	3.4	0.16–14.9	3.4	0.28–14.9	3.3	0.16–13.6
MBTCA	5.6	n.d.–56.9	6.8	n.d.–56.9	4.5	n.d.–24.5
Subtotal	11.6	0.26–87.2	13.0	0.45–87.2	10.3	0.26–43.7
β-caryophyllene (sesquiterpene) SOA tracers						
β-Caryophyllinic acid	2.9	0.16–17.2	3.5	0.17–17.2	2.3	0.16–9.6
Total measured tracers	22.9	1.1–135	23.6	1.4–135	22.2	1.1–115

[a] n.d. denotes not detected. [b] C_5-alkene triols: cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene and trans-2-methyl-1,3,4-trihydroxy-1-butene.

Table 2. Concentrations of organic carbon (OC) (ngC m^{-3}) from biogenic primary emission (biomass-burning OC and fungal-spore OC) and biogenic SOC and their contributions in aerosol OC (%) in marine aerosols over the East China Sea.

Component	Total			Daytime			Nighttime		
	Range	Mean	std	Range	Mean	std	Range	Mean	std
				Concentration (ngC m^{-3})					
Aerosol OC	424–14100	4260	3480	1030–14100	4940	3800	424–9830	3600	3080
Biomass burning OC	1.1–790	89.6	156	1.1–506	75.5	117	1.3–790	103	187
Fungal spore OC	1.2–1840	180	334	1.3–911	157	249	1.2–1840	203	403
Isoprene SOC [a]	0.78–324	39.8	55.4	2.3–133	32.1	37.6	0.78–324	47.2	68.3
Monoterpene SOC	1.1–377	50.2	72.0	1.9–377	56.1	84.3	1.1–189	44.6	58.9
Sesquiterpene SOC	6.9–747	126	153	7.4–747	153	183	6.9–416	100	114
Sum of biogenic SOC	11.3–1060	216	250	13.7–1060	241	279	11.3–824	192	222
Subtotal	16.1–3460	486	688	29.8–2480	473	600	16.1–3460	498	776
				Percentage in aerosol OC (%)					
Biomass burning OC	0.05–8.5	1.5	1.8	0.05–4.4	1.1	1.2	0.13–8.5	1.8	2.3
Fungal spore OC	0.03–19.8	3.1	4.0	0.03–16.6	2.6	3.7	0.18–19.7	3.5	4.2
Isoprene SOC	0.13–3.8	0.83	0.87	0.13–2.0	0.60	0.54	0.14–3.8	1.0	1.1
Monoterpene SOC	0.08–3.5	0.98	0.90	0.10–3.3	1.00	0.95	0.08–3.5	0.96	0.87
Sesquiterpene SOC	0.36–5.3	2.4	1.2	0.36–5.3	2.5	1.4	0.87–5.1	2.4	1.1
Sum of biogenic SOC	0.67–9.3	4.2	2.2	0.67–9.3	4.1	2.2	1.8–8.8	4.4	2.2
Subtotal	1.5–37.0	8.7	6.9	1.5–27.4	7.8	6.3	2.8–37.0	9.7	7.4

[a] The total mass concentrations of SOC produced by isoprene (2-methylglyceric acid and 2-methyltetrols were used), α/β-pinene, and β-caryophyllene were estimated using the tracer-based method by Kleindienst et al. (2007).

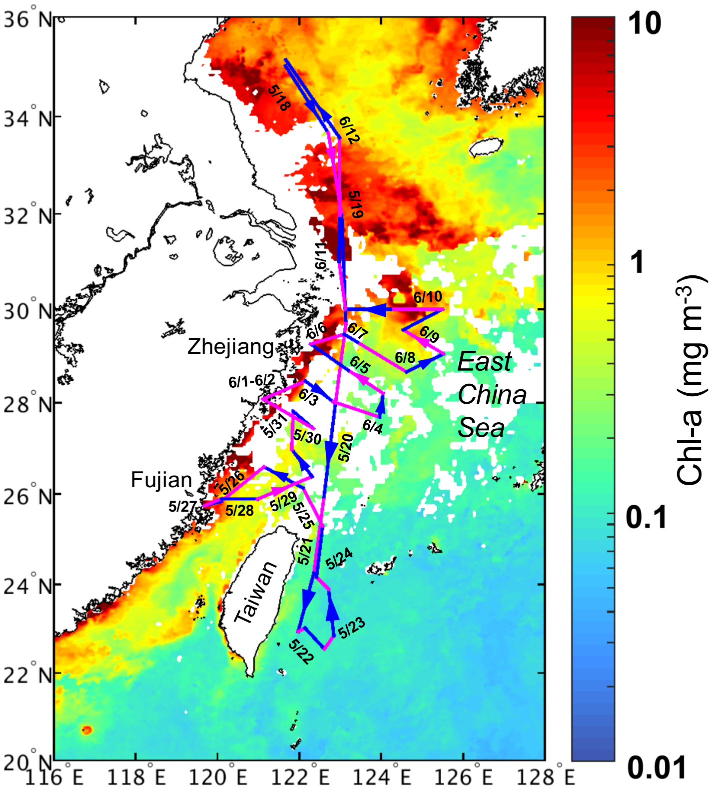

Figure 1. Cruise tracks of KEXUE-1 and spatial distribution of satellite-derived chlorophyll-a concentrations (chl-a, mg m^{-3}) in surface seawater derived from MODIS L3 products during the sampling period in the East China Sea. The purple and blue lines represent daytime and nighttime aerosol samples, respectively.

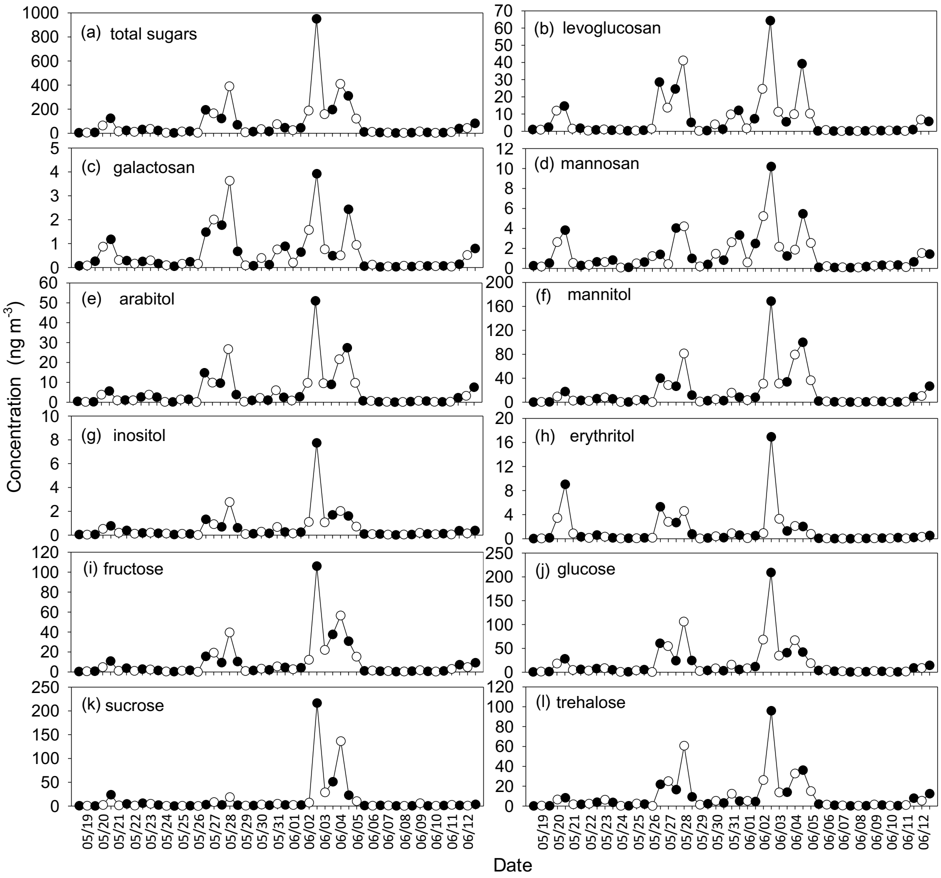

Figure 2. Temporal variations in sugar compounds in marine aerosols collected over the East China Sea. The open and shaded circles represent daytime and nighttime values, respectively.

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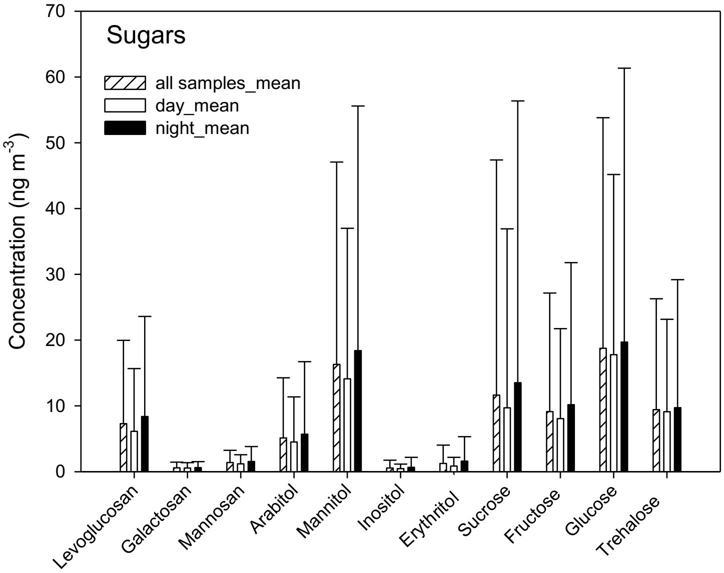


Figure 3. Average concentrations of sugars detected in marine aerosols over the East China Sea.

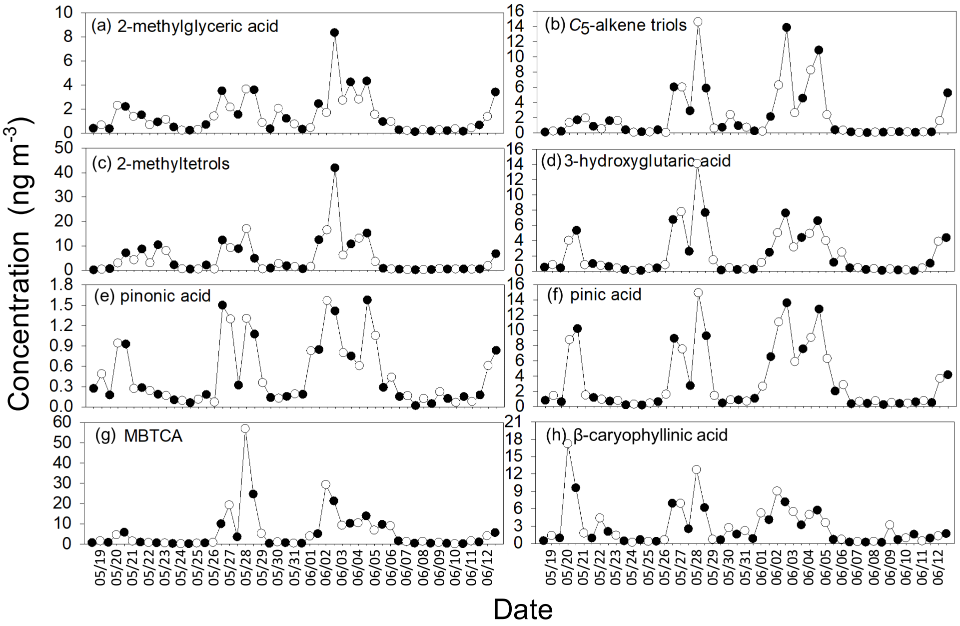


Figure 4. Temporal variations in biogenic SOA tracers detected in marine aerosols over the East China Sea during May to June 2014. The open and shaded circles represent daytime and nighttime values, respectively.

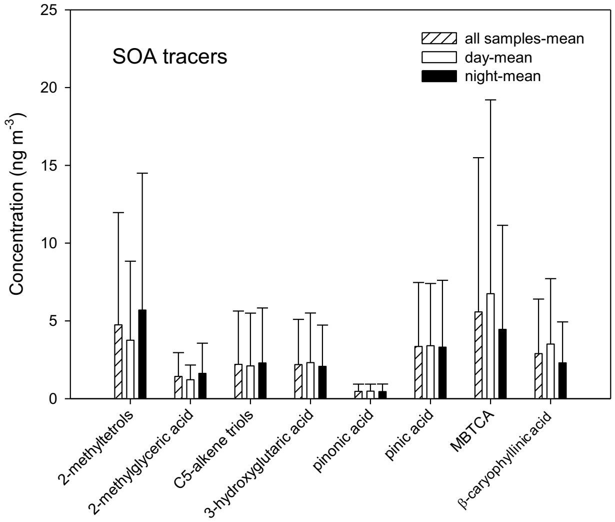


Figure 5. Average concentrations of SOA tracers detected in marine aerosols over the East China Sea.

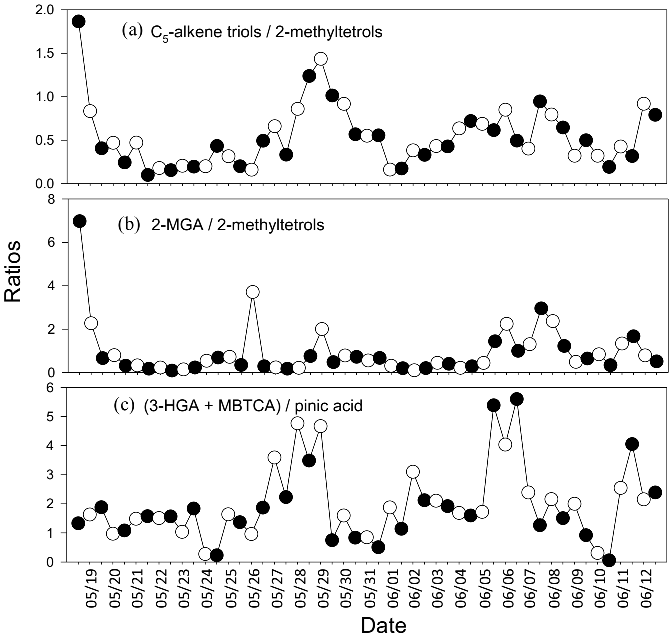


Figure 6. Temporal variations in the concentration ratios of isoprene and α/β-pinene oxidation products in the marine aerosols over the East China Sea. The open and shaded circles represent daytime and nighttime samples, respectively.

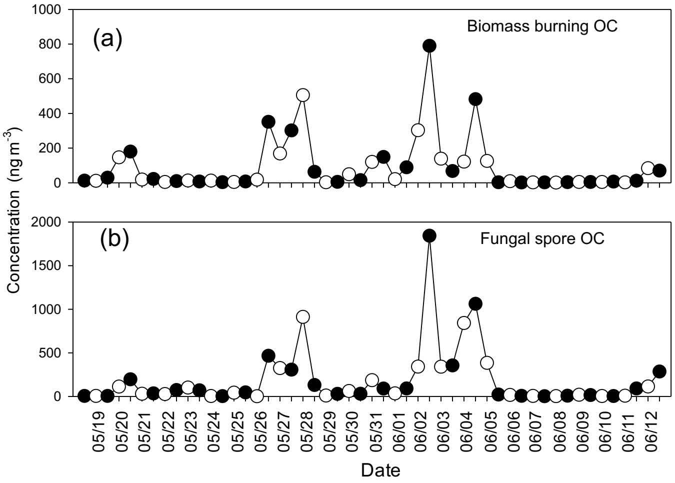


Figure 7. Temporal variations in (a) biomass-burning-derived OC, and (b) fungal-spore-derived OC in the marine aerosols over the East China Sea. The open and shaded circles represent daytime and nighttime samples, respectively.

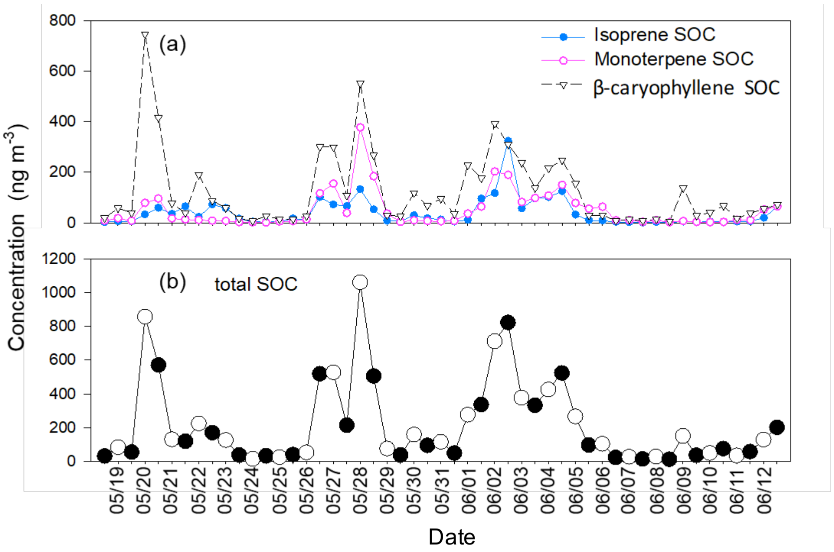


Figure 8. Temporal variations in (a) secondary organic carbon (SOC) derived from isoprene, α/β-pinene and sesquiterpene and (b) the total SOC levels in the marine aerosols over the East China Sea during May to June 2014. The open and shaded circles represent the daytime and nighttime samples, respectively.

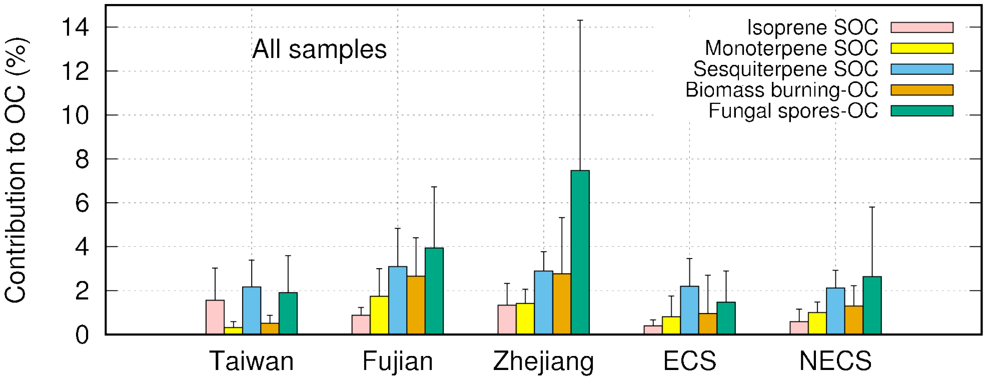


Figure 9. Contributions of OC (ngC m^{-3}) from biogenic primary emission (biomass-burning OC and fungal-spore OC) and biogenic SOC to OC (%) in different sampling regions. Taiwan, Fujian and Zhejiang refer to the waters around Taiwan, Fujian and Zhejiang; ECS represents East China Sea waters; NECS represents northern waters of ECS.

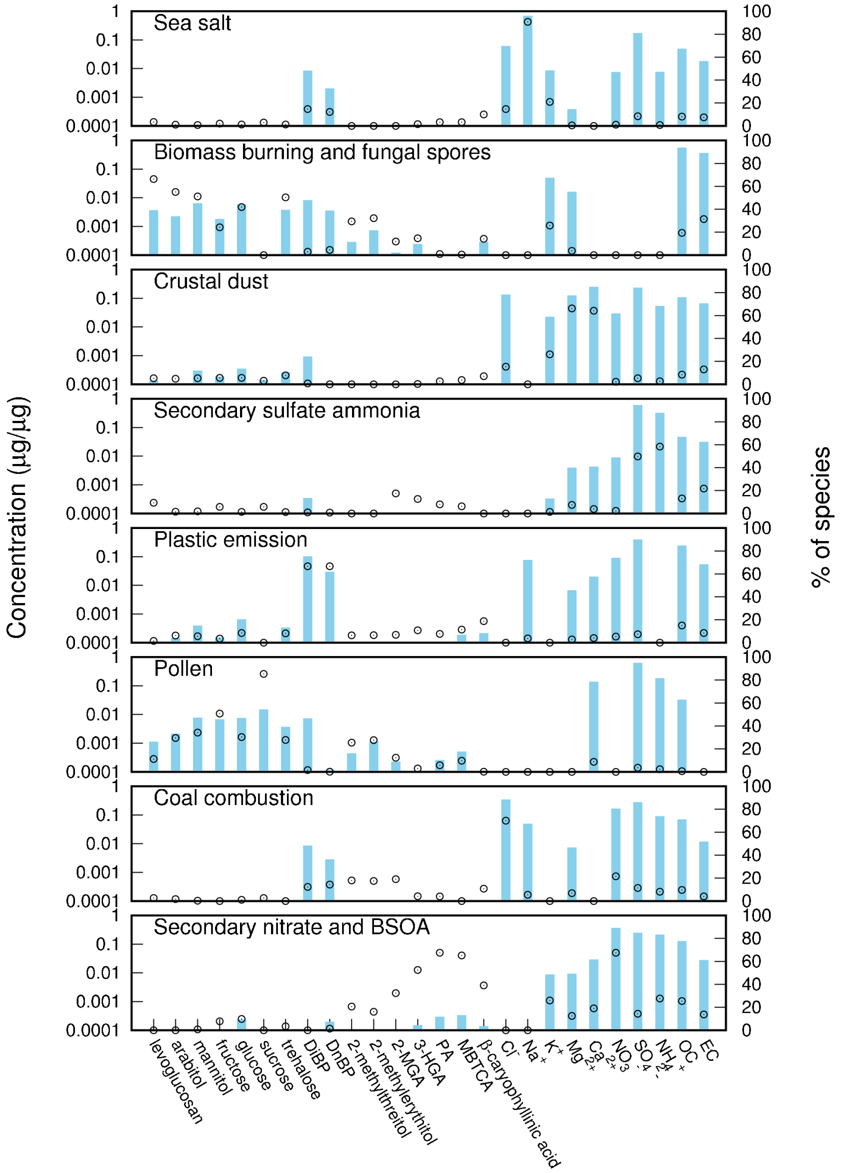


Figure 10. Source profiles identified by PMF. Blue bars represent the mass contribution with y-axis on the left, while black dots stand for the percentage of species to the sum with y-axis on the right.

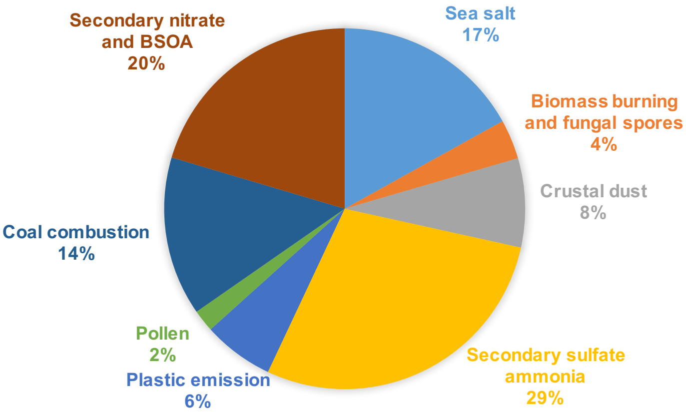
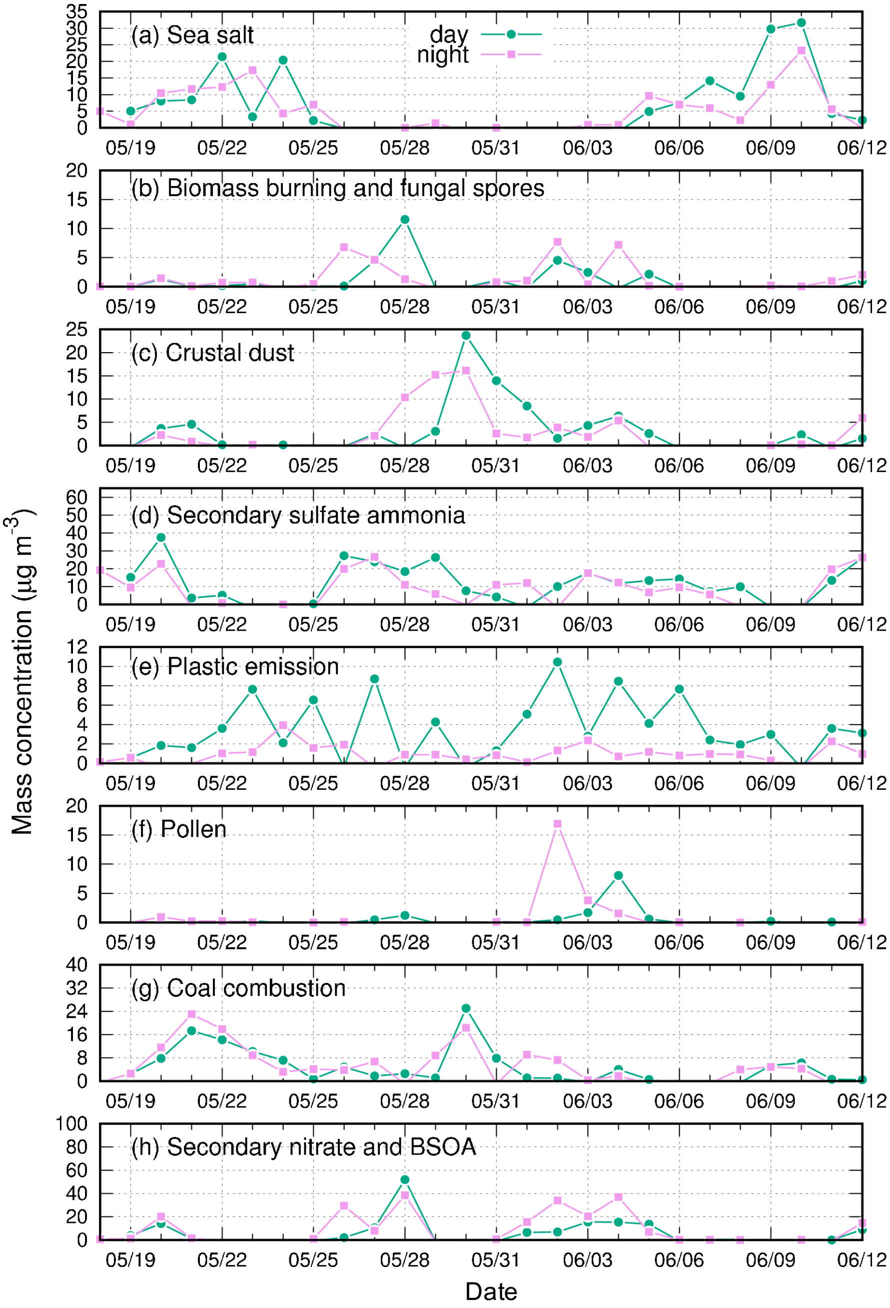


Figure 11. Contributions of different sources to marine organic aerosols over the East China Sea.



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1145 **Figure 12.** Temporal variation in sources contributed to marine aerosols (μg m^{-3}).