

### Molecular and spatial distributions of dicarboxylic acids, oxocarboxylic acids, and $\alpha$ -dicarbonyls in marine aerosols from the South China Sea to the eastern Indian Ocean

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Abstract. Marine aerosol samples collected from the South China Sea (SCS) to the eastern Indian Ocean (EIO) during a cruise from 10 March to 26 April 2015 were studied for diacids and related compounds. In view of air mass backward trajectories, source regions, and geographical features, the cruise area was categorized into the South China Sea (SCS), the eastern Indian Ocean off the coast of western Indonesia (EIO-WI), the EIO off the coast of Sri Lanka (EIO-SL), Malacca, and the Sri Lanka docking point (SLDP). Total concentrations of diacids, oxoacids, and  $\alpha$ -dicarbonyls were high at the SLDP, followed by the SCS and Malacca, and they were the low in the EIO-WI. In this study, oxalic acid  $(C_2)$ was the dominant diacid during the cruise, followed by malonic acid (C<sub>3</sub>) in the SCS, EIO-WI, EIO-SL, and Malacca, and succinic acid  $(C_4)$  was relatively more abundant than C<sub>3</sub> diacid at the SLDP. Except for SLDP, C<sub>3</sub>/C<sub>4</sub> mass ratios were always greater than 1, and no significant difference was observed during the cruise. The  $C_2/C_4$  and  $C_2/total$ diacid ratios also showed similar trends. The average mass ratios of adipic acid  $(C_6)$  to azelaic acid  $(C_9)$  were less than unity except for in the EIO-WI; the mass ratios of phthalic acid (Ph) to azelaic acid  $(C_9)$  were less than 2 except for in the SCS. The concentrations of diacids were higher when the air masses originated from terrestrial regions than when they originated from remote oceanic regions. Based on the molecular distributions of organic acids, the mass ratios, and the linear correlations of selected compounds in each area, we found that the oxidation of biogenic volatile organic compounds (BVOCs) released from the ocean surface and subsequent in situ photochemical oxidation was the main contributor to diacids, oxocarboxylic acids, and  $\alpha$ -dicarbonyls from the SCS to the EIO. In addition, the continental outflow, which is enriched in anthropogenic VOCs and their aged products, influenced the organic aerosol loading, particularly over the SCS. Emissions from Sri Lanka terrestrial vegetation as well as fossil fuel combustion and subsequent photochemical oxidation also played a prominent role in controlling the organic aerosol loading and the molecular distribution of diacids and related compounds at the SLDP.

#### 1 Introduction

Land-sea-air interaction is one of the most important issues in Earth system science. Atmospheric aerosols are one of the major components in the Earth's atmosphere and are the key carriers of the global biogeochemical cycle of nutrients (Zhuang et al., 1992; Li et al., 2017; Tan et al., 2011). Atmospheric aerosols containing inorganic and organic materials play a vital role in air quality, atmospheric chemistry, and the health of humans and ecosystems, and they have a critical impact on the global climate system (Ramanathan et al., 2001). Organic aerosols in tropospheric regions account for up to 90% of the total fine aerosol mass, and most of these aerosols are water soluble (Kanakidou et al., 2005). The abundant diacids, oxoacids, and  $\alpha$ -dicarbonyls are reported to be the major fraction of water-soluble organic aerosols (Sorooshian et al., 2010; Ervens et al., 2011; Cong et al., 2015); these water-soluble aerosols enhance the capacity of aerosol particles to act as cloud condensation nuclei and ice nuclei in the atmosphere (Ervens et al., 2011; D. Zhao et al., 2016; Vergara-Temprado et al., 2017; Huang et al., 2018), whereas water-insoluble substances such as lipid-class compounds can reduce their hygroscopic activity (Kawamura et al., 2017).

It has been well established that aerosols in the marine atmosphere are influenced by emissions from the ocean surface, such as plankton activity (Cavalli et al., 2004; O'Dowd and De Leeuw, 2007; Facchini et al., 2008). Marine-emitted aerosols account for more than half of the global natural aerosol burden (1000–3000 Tg yr<sup>-1</sup>; Iii and Duce, 1988); thus, they significantly influence the Earth's climate system (Haywood, 1999). Previous studies on marine aerosols have mainly focused on the measurement of non-sea-salt and seasalt sulfates (Charlson et al., 1987, 1992) and mineral dust (Schulz et al., 2012). However, diacids and related compounds in marine aerosols have been paid little attention, despite the fact that they account for more than 10% of total carbon (TC) in remote oceanic regions (Kawamura and Sakaguchi, 1999; Wang and Kawamura, 2006), which highlights their importance in the marine atmosphere.

Generally, molecular distributions of dicarboxylic acids in atmospheric aerosols are characterized by the dominance of oxalic ( $C_2$ ) acid, followed by malonic ( $C_3$ ) and succinic ( $C_4$ ) acids (Fu et al., 2013a; Kawamura and Bikkina, 2016). They can be directly emitted from anthropogenic emissions, such as fossil fuel combustion (Kawamura and Kaplan, 1987) and biomass burning (Narukawa et al., 1999; Kawamura et al., 2013), and can also be formed by the atmospheric oxidation of various volatile organic compounds (VOCs) emitted from primary sources (Kawamura et al., 1996a). In addition, unsaturated fatty acids emitted from oceanic biota can be further photo-oxidized to form the corresponding diacids in the atmosphere (Kawamura and Sakaguchi, 1999; Rinaldi et al., 2011). Isoprene, an abundant VOC from terrestrial higher plants as well as oceanic biota, is a major precursor of secondary organic aerosols (Lim et al., 2005; Carlton et al., 2009), including low-molecular-weight diacids such as  $C_{2-}$ C<sub>4</sub> (Nguyen et al., 2010).

Chemical characterization of dicarboxylic acids, oxoacids, and  $\alpha$ -dicarbonyls in atmospheric aerosols provides useful knowledge on the relative contribution of possible primary sources, the long-range atmospheric transport, and the photooxidation routes of organic compounds (Kawamura and Bikkina, 2016). Many studies have investigated the impacts of continental air outflows on the concentration, composition, and distribution of organic aerosols in marine regions (Fu et al., 2013a). For example, a long-term observation of aerosols on Chichijima Island in the western North Pacific found a remarkable increase in the concentrations of dicarboxylic acids in winter and spring due to the influence of the East Asian air outflow conveyed by the westerlies (Mochida et al., 2003a). Moreover, organic compounds such as unsaturated fatty acids from marine sources are main contributors to the secondary formation of diacids and related compounds in the ocean atmosphere (Miyazaki et al., 2010; Kawamura and Gagosian, 1987). Bikkina et al. (2014) found that the abundance of  $C_2$ – $C_6$  and  $C_9$  diacids continued to increase with the increase in phytoplankton activity in the North Pacific Ocean. Meanwhile, the oxidation products of isoprene (e.g. pyruvic and glyoxylic acids) observed in the marine boundary layer had a similar concentration trend to that of C<sub>2</sub>, suggesting that the secondary oxidation of biogenic VOCs from marine sources significantly contributes to the atmospheric loading of diacids and related compounds.

The oceans cover more than 70% of the Earth's surface, and marine aerosols are important components of the global aerosol system of natural sources. However, current knowledge about the biogeochemical cycles of organic matter in the tropical marine atmosphere is very limited. The South China Sea (SCS) is a large semi-closed marginal basin and one of the largest marginal seas in the world (Liu et al., 2002). The seasonal division of prevailing winds in the SCS is mainly influenced by the northeast monsoon from roughly mid-October to mid-March of the following year and by the southwest monsoon from mid-May to mid-September, while mid-March to mid-May is the spring transition period, during which the wind direction is variable. The climate of the SCS is part of the East Asian monsoon system (Lau et al., 1998). The Indian Ocean is the third largest ocean in the world, with distinct tropical maritime and monsoon climate characteristics. The prevailing wind over the Indian Ocean in summer is the southwest monsoon, while the prevailing wind in winter is the northeast monsoon (Fu et al., 2016; Ramanathan et al., 2005). The Indian Ocean is warmer than the Pacific and Atlantic oceans at the same latitude; thus, it is called the tropical ocean. The tropical eastern Indian Ocean (10° S-15° N, 65–100° E), including the southern Bay of Bengal, the southeastern Arabian Sea, the eastern equatorial Indian Ocean, and parts of the southern Indian Ocean, is one of the key regions affecting climate change, such as drought and flood, in China (Yao et al., 2015).

Although great progress has been made in the field of atmospheric organic aerosols, studies on diacids, oxoacids, and  $\alpha$ -dicarbonyls in the marine atmosphere are scarce and have been limited to the Mediterranean, the North Pacific, the South Pacific, the Caribbean, and the Atlantic Ocean (Kawamura and Bikkina, 2016); thus, little is known about marine aerosols over the Indian Ocean. Studies on the molecular composition and distribution of dicarboxylic acids and related compounds can provide useful information for source analysis as well as information regarding the secondary formation and photochemical transformation processes of atmospheric organic aerosols. In this study, total suspended particle (TSP) samples collected on a day- and night-time basis over the SCS and the EIO were studied for diacids, oxoacids, and  $\alpha$ -dicarbonyls, which provided an ideal opportunity to investigate the spatial distributions of marine organic aerosols influenced by organics from both marine emissions and long-range continental transport. In addition, carbonaceous components, i.e. organic carbon (OC), elemental carbon (EC), and water-soluble OC (WSOC), in the TSP samples were measured. Based on the molecular and spatial distributions, the mass ratios of organic compounds, and their relations with bulk components as well as backward air mass trajectories, we discuss their sources and possible formation pathways in the study region.

#### 2 Materials and methods

#### 2.1 Marine aerosol sampling

aerosol sampling was performed on Marine the R/V "Shiyan 1" during cruise NORC2015-10 in the SCS and the EIO (Fig. 1) from 10 March to 26 April 2015. TSP samples were collected at daytime (n = 44) and night-time (n = 43) using a high-volume air sampler (Kimoto AS-810A, KIMOTO, Japan) placed on the front upper deck of the vessel's navigation room. The exhaust outlet of the ship was located at the stern, and the aerosol samples were collected underway to avoid potential pollution from the ship's emissions. The three samples collected at the Sri Lanka docking point (SLDP) when the ship was docked in the port were seriously polluted by ship exhaust emission. Therefore, these three samples are discussed separately for comparison with the other samples. The air sampler was operated at a flow rate of  $1.0 \,\mathrm{m^3 \, min^{-1}}$  with pre-combusted (450 °C, 6 h) quartz filters (25 cm  $\times$  20 cm, Pallflex<sup>®</sup> TM, 2500 QAT-UP). We also collected field blanks (n = 4)during the cruise. After sampling, the filter samples were wrapped in aluminium foil, packed in zip-lock bags, and stored in the dark at -20 °C until the chemical analysis.

The 5d air mass backward trajectories arriving at 100 m a.s.l. (metres above sea level) each day were computed using the HYSPLIT (https://www.ready.noaa.gov/HYSPLIT. php, last access: 17 March 2019) model (Fig. 1). The air masses that arrived over the South China Sea (SCS) originated from East Asia and the surrounding oceanic regions. The air masses that arrived over the eastern Indian Ocean off the coast of western Indonesia (EIO-WI) originated from the remote EIO, whereas those that arrived over the eastern Indian Ocean off the coast of Sri Lanka (EIO-SL) were mixed from the remote EIO and the Bay of Bengal. The air masses that arrived over Malacca were from the Southeast Asian subcontinent and the surrounding EIO. In addition, the vessel



**Figure 1. (a)** Cruise tracks used for aerosol collection in the South China Sea (SCS) and the eastern Indian Ocean (EIO) from 10 March to 26 April 2015. The red line is located in the SCS region, the yellow line is in the eastern Indian Ocean near western Indonesia (EIO-WI), the green line is in the eastern Indian Ocean near Sri Lanka (EIO-SL), the blue line is in the Malacca region, and the red solid points are the collection positions of the three Sri Lanka docking point (SLDP) samples. The base map (© MAT-LAB) reflects an average composite of Chlorophyll *a* concentrations from March to April 2015 obtained from the NASA website: https://modis.gsfc.nasa.gov/data/dataprod/chlora.php (last access: 3 July 2019). (b) Air mass backward trajectories for the sampling days at an arrival height of 100 m; the map was produced using © MeteoInfo software. (Please note that the above figure contains disputed territories.)

was docked at the Sri Lanka docking point (SLDP) for 3 d, during which the air masses were mainly from the surrounding oceanic regions. Thus, the aerosol samples collected in these different locales during the cruise may have been affected by long-range atmospheric transport; hence, we segregated the TSP samples into five categories: SCS, EIO-WI, EIO-SL, Malacca, and SLDP (Fig. 1).

#### 2.2 Determination of diacids and related compounds

Aerosol samples were determined for water-soluble organic acids using a previously reported method (Kawamura, 1993). Briefly, small pieces (47 mm in diameter) of TSP filter samples were extracted three times using organic-free Milli-Q water (10 mL) under ultrasonication. The extracts were then concentrated to dryness and reacted with 14 % BF<sub>3</sub>/n-butanol at 100 °C for 1 h. The derivatized acids and carbonyls were extracted with *n*-hexane and injected into a split/splitless gas chromatograph (GC-FID, Agilent 6980) equipped with a HP-5 column for the determination of diacids and related compounds. The field blank filters were also analysed using the same experimental procedure. Recoveries of major organic acids were better than 85 %. The analytical errors in the duplicate analysis were within 10% for major species. Concentrations of diacids and related compounds were corrected according to the field blanks.

#### 2.3 Measurements of WSOC, OC, and EC

For WSOC measurement, 17.3 or 34.7 cm<sup>2</sup> of each filter was extracted with Milli-Q water (20 mL) under ultrasonication for 20 min; the extracts were analysed using a total organic carbon (TOC) analyser (TOC-L, 5000A, Shimadzu, Japan). OC and EC were determined by a carbon analyser (Sunset Laboratory Inc., USA), using a piece ( $1.5 \text{ cm}^2$ ) of each filter, following the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol (Pavuluri et al., 2011). The limits of detection (LODs) for both OC and EC were 0.1 µg C cm<sup>-2</sup> with a precision of greater than 10 %. The concentrations of all of the carbonaceous components reported here were corrected using the field blanks.

Table 1 shows the concentration levels of OC and EC in TSP samples collected from different marine regions. The concentration of EC  $(4.24 \pm 3.02 \,\mu g \,m^{-3})$  in the SLDP aerosols was much higher than the concentrations in other regions (SCS was  $0.27 \pm 0.15 \,\mu g \,m^{-3}$ , EIO-WI was  $0.05 \pm 0.05 \,\mu g \,m^{-3}$ , EIO-SL was  $0.04 \pm 0.18 \,\mu g \,m^{-3}$ , and Malacca was  $0.24 \pm 0.18 \,\mu g \,m^{-3}$ ), which proved that the SLDP samples were seriously polluted by ship exhaust, but pollution from exhaust in other sea areas should be minor.

#### **3** Results and discussion

# **3.1** OC, EC, and WSOC concentrations in marine aerosols

The concentrations of OC, EC, and WSOC in each marine region (SCS, EIO-WI, EIO-SL, Malacca, and SLDP) are summarized in Table 1. In the samples collected from the SCS to the EIO from March to April 2015, the mass concentrations of OC and EC varied from 0.02 to  $20.9 \,\mu g \,m^{-3}$ (mean of  $1.29\pm2.72\,\mu g\,m^{-3})$  and from 0.00 to  $7.57\,\mu g\,m^{-3}$ (mean of  $0.33 \pm 0.90 \,\mu\text{g m}^{-3}$ ) respectively. Generally, the mass concentrations of OC and EC at the SLDP were the highest, followed by Malacca and SCS, and the lowest values were found in the EIO-WI and EIO-SL. In this study, the mean mass concentrations of OC and EC in the SCS were 1.5 times (OC mean of  $0.82 \,\mu g \,m^{-3}$ ) and 1.7 times (EC mean of  $0.16 \,\mu\text{g}\,\text{m}^{-3}$ ) higher than those reported by Fu et al. (2013a) in the SCS in late February 1990. As the sampling season was the same, the above situation indicated that the input of anthropogenic emissions to the SCS carbon aerosols was increasing with the economic development of the areas surrounding the SCS. The mass concentrations of OC and EC in the SCS were lower than those in the western SCS (OC of  $2.04 \,\mu g \,m^{-3}$  and EC of  $3.0 \,\mu g \,m^{-3}$ ) which were strongly affected by biomass burning (Song et al., 2018). In addition, the carbonaceous aerosol levels in Malacca were similar to those in the Bay of Bengal (OC of  $1.9 \,\mu g \,m^{-3}$  and EC of  $0.4 \,\mu g \, m^{-3}$ ; Kumar et al., 2008). The concentrations of carbon components at the SLDP were relatively close to that of Jeju Island (OC of  $11.3 \,\mu g \,m^{-3}$  and EC of  $3.0 \,\mu g \,m^{-3}$ ; Jung and Kawamura, 2011), and were higher than that of Sapporo Island (OC of  $6.1 \,\mu g \, m^{-3}$  and EC of  $1.9 \,\mu g \, m^{-3}$ ; Simoneit et al., 2004); the above-mentioned two sites were greatly affected by terrestrial long-range transmission. Meanwhile, the concentrations of carbon components in the EIO-WI and EIO-SL were lower than those in the northern Atlantic (OC of  $0.93 \,\mu g \,m^{-3}$  and EC of  $0.27 \,\mu g \,m^{-3}$ ; Zhang et al., 2010), the Pacific (OC of  $0.82 \,\mu g \,m^{-3}$  and EC of  $0.22 \,\mu g \,m^{-3}$ ; Zhang et al., 2010), Amsterdam Island (OC of  $0.24 \,\mu g \, m^{-3}$ and EC not detected; Claeys et al., 2010), the Arctic Ocean (OC of  $0.56 \,\mu\text{g m}^{-3}$ ; Fu et al., 2013b), and so on. These locations were all less affected by terrestrial anthropogenic emissions. The concentration levels of carbonaceous components in the EIO-WI and EIO-SL were lower than those in the Indian Ocean (OC of  $0.71\,\mu g\,m^{-3}$  and EC of  $0.49\,\mu g\,m^{-3};\,Fu$ et al., 2011).

EC is the product of residential coal combustion, fossil fuel combustion, and the incomplete combustion of biomass, whereas OC contains both primary organic carbon and secondary organic aerosol generated by the photochemical reactions of organic gases in the atmosphere. The concentration of EC in SLDP aerosol ( $4.24 \pm 3.02 \,\mu g \,m^{-3}$ ) was much higher than that in other marine areas (SCS was  $0.27 \pm 0.15 \,\mu g \,m^{-3}$ , EIO-WI was  $0.05 \pm 0.05 \,\mu g \,m^{-3}$ , EIO-SL was

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Species	SCS (	n = 27	EIO-WI	(n = 20)	EIO-SL	(n = 28)	Malacci	(n = 6)	SLDP	(n = 3)
	Range	Mean $\pm$ SD	Range	$\mathrm{Mean}\pm\mathrm{SD}$	Range	$Mean\pm SD$	Range	$\text{Mean}\pm\text{SD}$	Range	Mean $\pm$ SD
Dicarboxylic acids										
Oxalic, C <sub>2</sub>	30.3-626	$233 \pm 143$	4.43-70.1	$18.2\pm18.4$	5.21-232	$58.2 \pm 55.3$	14.5–373	$145 \pm 112$	179-454	$303 \pm 140$
Malonic, C <sub>3</sub>	2.14 - 87.9	$36 \pm 23$	0.34 - 11.4	$2.09 \pm 2.52$	0.76 - 42.1	$8.19\pm9.95$	2.57-74.0	$24.2 \pm 25.4$	25.9–55.4	$42.2 \pm 15.0$
Succinic, C <sub>4</sub>	1.73 - 50.4	$18 \pm 14$	0.23 - 6.4	$1.35\pm1.65$	0.57 - 20.6	$4.33 \pm 4.86$	1.18 - 72.9	$18.0\pm22.7$	14.1 - 78.5	$45.2 \pm 32.2$
Glutaric, $C_5$	0.23 - 8.52	$2.60 \pm 2.15$	bdl-0.79	$0.23\pm0.19$	bdl-1.69	$0.48\pm0.46$	bdl-9.53	$3.49 \pm 3.70$	2.94 - 14.6	$8.82\pm5.85$
Adipic, $C_6$	0.13 - 4.09	$1.11 \pm 0.93$	0.17 - 0.83	$0.42 \pm 0.22$	0.03 - 1.18	$0.31\pm0.29$	0.01 - 3.59	$1.28\pm1.36$	1.95 - 7.17	$4.76\pm2.63$
Pimelic, $C_7$	bdl-1.88	$0.58\pm0.60$	bdl-0.22	$0.03\pm0.07$	bdl-0.50	$0.12 \pm 0.17$	bdl-1.30	$0.43 \pm 0.46$	bdl-0.45	$0.28\pm0.25$
Suberic, C <sub>8</sub>	lbdl	lbd	bdl-0.09	$0.004\pm0.02$	bdl-14.3	$0.51 \pm 2.71$	lbd	lpql	lbd	lþdl
Azelaic, C <sub>9</sub>	bdl-6.97	$1.82 \pm 1.57$	bdl-2.22	$0.45\pm0.49$	0.09 - 15.1	$1.25\pm2.75$	0.32 - 3.96	$1.82\pm1.29$	11.7 - 140	$68.9\pm65.1$
Sebacic, C <sub>10</sub>	bdl-2.69	$0.28\pm0.53$	bdl-0.82	$0.29\pm0.24$	bdl-9.06	$0.57\pm1.68$	bdl-1.10	$0.58\pm0.46$	0.66 - 3.43	$2.00\pm1.39$
Undecanedioic, C <sub>11</sub>	bdl-0.16	$0.02\pm0.05$	bdl-0.69	$0.16\pm0.15$	bdl-0.38	$0.13\pm0.10$	bdl-0.38	$0.20\pm0.15$	bdl-1.64	$0.62\pm0.89$
Dodecanedioic, C <sub>12</sub>	lbdl	bdl	bdl-0.35	$0.02\pm0.08$	lbd	lbdl	bdl-0.29	$0.06 \pm 0.11$	lbd	lbdl
Methylmalonic, iC <sub>4</sub>	bdl-2.26	$0.95\pm0.65$	bdl-0.29	$0.01\pm0.06$	bdl-0.82	$0.14\pm0.23$	bdl-3.29	$0.93 \pm 1.06$	1.02 - 2.47	$1.94\pm0.79$
Methylsuccinic, iC <sub>5</sub>	0.30 - 3.37	$1.46\pm0.98$	0.08 - 0.54	$0.35\pm0.12$	0.13 - 1.18	$0.56\pm0.30$	0.21 - 3.56	$1.63 \pm 1.28$	2.61 - 10.1	$6.99\pm3.89$
Methylglutaric, iC <sub>6</sub>	bdl-0.68	$0.05\pm0.18$	bdl-0.18	$0.02 \pm 0.05$	lbd	lbd	bdl-0.59	$0.26\pm0.25$	0.67 - 3.29	$1.84\pm1.33$
Maleic, M	0.12 - 2.70	$0.93\pm0.67$	0.07-0.55	$0.19\pm0.11$	0.08 - 1.02	$0.28\pm0.22$	0.04 - 1.42	$0.77\pm0.59$	1.58 - 4.14	$2.56\pm1.38$
Fumaric, F	0.17 - 2.16	$0.74\pm0.48$	0.16 - 1.45	$0.77\pm0.32$	0.05 - 0.82	$0.28\pm0.22$	0.08 - 1.07	$0.39\pm0.33$	0.81 - 2.49	$1.49\pm0.89$
Methylmaleic, mM	0.17 - 2.13	$0.82\pm0.48$	0.17 - 0.76	$0.39\pm0.15$	0.06-0.96	$0.32 \pm 0.21$	0.11 - 1.33	$0.73\pm0.47$	2.26-5.49	$3.80\pm1.62$
Phthalic, Ph	0.16 - 6.57	$2.29 \pm 1.89$	bdl-1.25	$0.50\pm0.34$	0.06 - 2.95	$0.77 \pm 0.59$	0.26 - 3.56	$1.64 \pm 1.23$	8.63–13.2	$10.8\pm2.31$
Isophthalic, iPh	bdl-0.60	$0.05\pm0.16$	bdl-0.37	$0.02 \pm 0.08$	bdl-0.22	$0.02 \pm 0.06$	bdl-0.49	$0.12 \pm 0.20$	1.08 - 2.73	$1.99\pm0.84$
Terephthalic, tPh	bdl-2.12	$0.22\pm0.57$	bdl-1.25	$0.13 \pm 0.17$	bdl-0.38	$0.03 \pm 0.09$	bdl-0.59	$0.10\pm0.21$	bdl-1.76	$0.59\pm1.02$
Malic, hC <sub>4</sub>	bdl-2.25	$0.62\pm0.53$	bdl-0.72	$0.05\pm0.17$	bdl-0.81	$0.13 \pm 0.23$	bdl-1.05	$0.31\pm0.35$	0.88 - 1.95	$1.45\pm0.54$
Ketomalonic, kC <sub>3</sub>	bdl-5.84	$1.76\pm1.34$	bdl-0.83	$0.22 \pm 0.22$	0.05 - 2.10	$0.54\pm0.47$	0.15 - 2.19	$1.00 \pm 0.90$	1.15 - 2.75	$2.06\pm0.82$
4-Ketopimelic, kC7	bdl-7.75	$1.85\pm1.70$	bdl-0.63	$0.12\pm0.19$	bdl-1.87	$0.45\pm0.56$	0.17 - 9.27	$3.59\pm3.68$	1.24 - 3.34	$2.50\pm1.10$
Subtotal	44.6–759	$305 \pm 186$	8.28–96.3	$26.1 \pm 23.3$	8.55–294	$77.6 \pm 73.1$	21.9–501	$207 \pm 158$	259–708	$514 \pm 231$
Oxocarboxylic acids										
Pyruvic, Pyr	0.01-1.70	$0.60 \pm 0.42$	bdl-0.70	$0.30 \pm 0.17$	0.11-0.75	$0.33 \pm 0.19$	bdl-1.23	$0.46 \pm 0.44$	0.83-1.62	$1.13 \pm 0.42$
Glyoxylic, $\omega C_2$	0.41 - 9.23	$2.68\pm1.87$	bdl-0.75	$0.23\pm0.23$	0.09 - 2.89	$0.97\pm0.86$	0.003 - 4.92	$2.05\pm2.08$	3.56-8.65	$6.28\pm2.56$
3-Oxopropanoic, <i>w</i> C <sub>3</sub>	0.14 - 2.53	$0.86\pm0.56$	0.06 - 0.65	$0.27\pm0.14$	bdl-0.75	$0.25\pm0.26$	bdl-2.01	$0.56\pm0.61$	0.55 - 2.16	$1.13 \pm 0.90$
4-Oxobutanoic, $\omega C_4$	bdl-1.09	$0.29\pm0.41$	bdl	bdl	bdl-1.42	$0.06\pm0.27$	bdl-2.66	$0.72 \pm 1.02$	1.41 - 9.27	$5.10 \pm 3.95$
5-Oxopentanoic, $\omega C_5$	bdl-0.09	$0.01\pm0.03$	0.05 - 0.39	$0.13\pm0.08$	bdl-0.15	$0.04 \pm 0.03$	bdl-0.15	$0.04\pm0.05$	0.07 - 0.21	$0.16\pm0.07$
7-Oxoheptanoic, $\omega C_7$	bdl-0.23	$0.23\pm0$	lbd	bdl	lbd	lbdl	lbd	lbd	lbd	lbd
8-Oxooctanoic, $\omega C_8$	bdl-3.94	$1.37 \pm 1.44$	lbd	bdl	lbd	lbd	bdl-0.23	$0.07 \pm 0.10$	bdl-16.1	$8.47 \pm 8.07$
9-Oxononanoic, $\omega C_9$	bdl-1.89	$0.69\pm0.65$	bdl-0.29	$0.03\pm0.07$	bdl-1.41	$0.19\pm0.36$	bdl-0.88	$0.32 \pm 0.32$	0.80-2.38	$1.72 \pm 0.83$
Subtotal	1.48 - 13.2	$6.51 \pm 3.99$	0.16 - 2.01	$0.96\pm0.46$	0.23 - 5.06	$1.85 \pm 1.51$	0.29 - 10.4	$4.22 \pm 3.75$	7.46-40.3	$24.0 \pm 16.4$

Species	SCS (	n = 27)	EIO-WI	(n = 20)	EIO-SL	(n = 28)	Malacc	n (n = 9)	SLDP	(n = 3)
	Range	Mean $\pm$ SD								
$\alpha$ -dicarbonyls										
Glyoxal, Gly	0.05-7.70	$2.28\pm2.26$	0.20-3.20	$1.64\pm0.67$	0.11-2.02	$0.87\pm0.40$	0.26-0.87	$0.52\pm0.23$	2.70-7.04	$4.15\pm2.50$
Methylglyoxal, MeGly Subtotal	0.29-20.0 0.56-20.2	$2.97 \pm 3.72$ $5.25 \pm 4.46$	0.88–3.01 1.08–5.29	$1.66 \pm 0.54$ $3.31 \pm 1.01$	0.09–7.45 0.95–8.86	$1.22 \pm 1.31$ $2.08 \pm 1.47$	0.93–4.01 1.18–4.79	$1.81 \pm 0.93$ $2.34 \pm 1.06$	2.31–4.45 5.04–11.5	$3.20 \pm 1.11$ $7.35 \pm 3.58$
Carbonaceous compone:	nts									
OC	0.18-2.63	$1.26\pm0.67$	0.02-0.66	$0.27\pm0.19$	0.06-1.69	$0.59\pm0.45$	0.28-4.44	$2.02\pm1.54$	3.57-20.9	$12.8\pm8.73$
EC	0.05 - 0.75	$0.27\pm0.15$	0.01 - 0.13	$0.05\pm0.05$	0.04 - 0.91	$0.21\pm0.18$	0.07 - 0.63	$0.24\pm0.18$	1.67-7.57	$4.24\pm3.02$
WSOC	0.22 - 2.31	$1.05\pm0.65$	0.05 - 0.58	$0.15\pm0.12$	0.06 - 1.00	$0.35\pm0.25$	0.09–2.72	$1.15\pm0.92$	1.12–7.44	$4.43 \pm 3.17$
				3						

"bdl" represents that a compound was below the limit of detection, which is ca.  $0.005 \text{ ng m}^{-3}$  for the target compounds

 $0.21 \pm 0.18 \,\mu g \, m^{-3}$ , and Malacca was  $0.24 \pm 0.18 \,\mu g \, m^{-3}$ ), indicating that the aerosol samples from the SLDP were seriously polluted by ship exhaust, but the other marine samples were not. OC and EC can roughly determine the source of aerosols. There was a weak correlation between the concentration of OC and EC in aerosols from the SCS to the EIO ( $R^2 = 0.34$ , P < 0.001), indicating that the origins of organic aerosols were different from those of EC and were affected by multiple sources (Turpin and Huntzicker, 1995). In addition, the OC / EC ratio can be used to indicate the contribution of different sources (Chow et al., 1996). The contribution of different emission sources, the influence of secondary organic aerosol formation, and the removal path of OC and EC can all affect the OC / EC ratio. When the OC / EC ratio is greater than 2, it indicates the presence of secondary organic aerosols. The OC / EC ratio was  $5.52 \pm 5.33$  (range of 1.02–29.7) in the SCS,  $11.84 \pm 17.44$  (range of 1.55– 51.0) in the EIO-WI,  $0.96 \pm 2.33$  (range of 0.96–9.28) in the EIO-SL,  $8.76 \pm 6.84$  (range of 2.71–24.4) in Malacca, and  $2.98 \pm 0.97$  (range of 2.14–4.04) at the SLDP. Among these values, the ratio of OC / EC in the SCS was very similar to that measured by Fu et al. (2013a) in TSP samples collected in the SCS (OC / EC: 5.1). The above results indicate that the contribution of secondary organic aerosols was widespread in aerosol samples from the SCS to the EIO, except for some samples in EIO-WI and EIO-SL. The concentrations of WSOC were highest (range of 1.12-7.44 ng m<sup>-3</sup> and mean of  $4.43 \pm 3.17$  ng m<sup>-3</sup>) at the SLDP followed by Malacca (range of 0.09-2.72 ng m<sup>-3</sup> and mean

of  $1.15 \pm 0.92$  ng m<sup>-3</sup>), the SCS (range of 0.22-2.31 ng m<sup>-3</sup> and mean of  $1.05 \pm 0.65$  ng m<sup>-3</sup>), the EIO-SL (range of 0.06–1.00  $ng\,m^{-3}$  and mean of 0.35  $\pm$  0.25  $ng\,m^{-3}),$  and the EIO-WI (range of 0.05–0.58  $\mathrm{ng}\,\mathrm{m}^{-3}$  and mean of 0.15  $\pm$  $0.12 \text{ ng m}^{-3}$ ). The WSOC concentrations from the SCS to EIO are much lower than those in urban aerosols from Tokyo (mean of  $13 \,\mu g \, m^{-3}$ ; Sempéré and Kawamura, 1994) and in biomass burning aerosols from Amazonia  $(18-51 \,\mu g \, m^{-3})$ ; Kundu et al., 2010a). However, WSOC concentrations in the EIO-SL are comparable to those reported in marine aerosols from the central Pacific (mean of  $0.30 \,\mu g \,m^{-3}$ ; Hoque and Kawamura, 2016), the western Pacific (mean of  $0.33 \,\mu g \,m^{-3}$ ; Sempéré and Kawamura, 2003), and Hawaii (mean of  $0.39 \,\mu g \,m^{-3}$ ; Hoffman and Duce, 2013). Kawamura et al. (2010) determined lower WSOC concentrations (range of  $0.04-0.30 \,\mu\text{g m}^{-3}$  and a mean of  $0.18 \,\mu\text{g m}^{-3}$ ) in Arctic aerosols, which are comparable to those observed in the EIO-WI.

### **3.2** Concentrations and molecular distributions of dicarboxylic acids and related compounds

The concentrations of dicarboxylic acids, oxocarboxylic acids, and  $\alpha$ -dicarbonyls in each marine region (the SCS, EIO-WI, EIO-SL, Malacca, and the SLDP) are summarized in Table 1. Their chemical structures are shown in Fig. S1

Table 1. Continued



Figure 2. Molecular distributions of dicarboxylic acids and related compounds in TSP samples from the (a) SCS, (b) EIO-WI, (c) EIO-SL, (d) Malacca, and (e) SLDP from 10 March to 26 April 2015.

in the Supplement. Most of the organic species were found to be more abundant at the SLDP followed by the SCS, Malacca, the EIO-WI, and the EIO-SL (Table 1). For the aerosol samples from the SCS, the 5d backward trajectories (Fig. 1b) showed that the air masses originated from East Asia, whereas the air masses that arrived at Malacca were delivered from Southeast Asia. The concentrations of diacids and related compounds were highest in the SCS followed by Malacca, due to increased anthropogenic inputs conveyed by long-range atmospheric transport from East Asia (Y. Zhao et al., 2016) and Southeast Asia respectively. The C<sub>2</sub> diacid showed the highest abundance, with the abundance of the other components (see Table 1 for full component abbreviations) showing the following orders for the different locations:  $C_3 > C_4 > MeGly > \omega C_2 > C_5 > Ph \approx$ Gly > C<sub>9</sub> over the SCS (Fig. 2a);  $C_3$  > MeGly >  $C_4$  > F >

Ph > C<sub>6</sub>  $\approx$  C<sub>9</sub> over the EIO-WI (Fig. 2b); C<sub>3</sub> > C<sub>4</sub> > C<sub>9</sub>  $\approx$  MeGly >  $\omega$ C<sub>2</sub> > Gly > Ph over the EIO-SL; and C<sub>2</sub> > C<sub>3</sub> > C<sub>4</sub> > kC<sub>7</sub> > C<sub>5</sub> >  $\omega$ C<sub>2</sub> > C<sub>9</sub>  $\approx$  MeGly over Malacca. The dominance of C<sub>2</sub> followed by the C<sub>3</sub> and C<sub>4</sub> diacids is consistent with coastal marine aerosols (Kundu et al., 2010b; Kunwar and Kawamura, 2014) and remote marine aerosols from the western North Pacific (Bikkina et al., 2015), suggesting similar formation processes for dicarboxylic acids in the atmosphere of coastal or remote regions.

Table 1 shows the total concentrations of diacids in marine aerosols from the five regions in this study (the SCS was  $0.27\pm0.15$  ng m<sup>-3</sup>, the EIO-WI was  $0.05\pm0.05$  ng m<sup>-3</sup>, the EIO-SL was  $0.04\pm0.18$  ng m<sup>-3</sup>, Malacca was  $0.24\pm0.18$  ng m<sup>-3</sup>, and the SLDP was  $0.27\pm0.15$  ng m<sup>-3</sup>). Fu et al. (2013a) reported that the mean concentrations of total diacids in marine aerosol samples in the SCS and the

Indian Ocean were 489 and  $301 \text{ ng m}^{-3}$  respectively. By comparison of this study with aerosols from other marine areas, it was found that the mean concentration of total diacids in the EIO was similar to that in the western Pacific Ocean ( $60 \pm 39$  ng m<sup>-3</sup>; Wang et al., 2006). Furthermore, the concentrations of total diacids from the five sea areas in this study were all lower than that reported for the East China Sea ( $850 \text{ ng m}^{-3}$ ; Mochida et al., 2003b) and higher than that reported for the Southern Ocean  $(4.5 \pm 4.0 \text{ ng m}^{-3})$ ; Wang et al., 2006). In addition, the concentrations of total diacids in aerosol samples in all sea areas in this study were higher than that reported at Alert in the Canadian High Arctic ( $25 \text{ ng m}^{-3}$ ; Kawamura et al., 1996a) and lower than that reported in urban aerosol from Xi'an, China, during different dust events  $(932-2240 \text{ ng m}^{-3}; \text{ Wang et al.},$ 2015) and in aerosol in the megacity of Chennai in India  $(694.5 \pm 176.3 \text{ and } 640.6 \pm 150.6 \text{ ng m}^{-3} \text{ in early and late}$ winter respectively and in summer  $502.9 \pm 117.9$  ng m<sup>-3</sup>; Pavuluri et al., 2010). Combined with the geographical location of the SLDP and the fact that the samples were collected in the ship's docking port, it is speculated that the organic aerosol samples from SLDP may have been affected by local coastal and terrestrial biological sources and anthropogenic emissions (especially fossil fuel combustion). The diacid abundance order ( $C_2 > C_9 > C_4 > C_3 > Ph > C_5$ ) observed at SLDP was similar to that reported in continental aerosols (Kawamura and Bikkina, 2016).

#### 3.2.1 Dicarboxylic acids

C<sub>2</sub>-C<sub>4</sub>, C<sub>6</sub>, C<sub>9</sub>, and phthalic (Ph) acids are important species of dicarboxylic acids; this section briefly summarizes the main sources and/or formation processes of these organic acids. C2 diacid concentrations ranged from 4.43 to 70.1 ng m<sup>-3</sup> with a mean of  $18.2 \pm 18.4$  ng m<sup>-3</sup> in the EIO-WI, from 5.21 to  $232 \text{ ng m}^{-3}$  with a mean of  $58.2\pm55.3$  ng m^{-3} in the EIO-SL, from 14.5 to 373 ng m^{-3} with a mean of  $145 \pm 112$  ng m<sup>-3</sup> in Malacca, from 30.3 to 626 ng m<sup>-3</sup> with a mean of  $233\pm143$  ng m<sup>-3</sup> in the SCS, and from 179 to  $454 \text{ ng m}^{-3}$  with a mean of  $303 \pm 140 \text{ ng m}^{-3}$ at the SLDP. It can clearly be seen that the concentrations of C<sub>2</sub> acid in the SCS and Malacca were higher than those in the EIO-SL and EIO-WI (Table 1). This large amount of C<sub>2</sub> could have been generated from the following sources: fossil fuel combustion (Kawamura and Kaplan, 1987; Donnelly et al., 2010), biomass combustion (Schauer et al., 2001; Narukawa et al., 1999), cooking emissions (Kawamura and Kaplan, 1987; Rogge et al., 1993), and the photooxidation of VOCs and other precursors (Kawamura and Yasui, 2005; Kundu et al., 2010b). The diurnal variation trend of C<sub>2</sub> acid was similar to that of C<sub>3</sub> and C<sub>4</sub> acids, indicating that these compounds may have had similar photochemical oxidation pathways or emission sources in the atmosphere.

 $C_9$  diacid was found to be the most abundant diacid in the range of  $C_7$ – $C_{11}$  diacids, which is similar to findings on ma-

rine aerosols from the southern and western Pacific Ocean (Wang et al., 2006). Such a high abundance of C<sub>9</sub> diacid indicates that marine biogenic emissions and the subsequent photochemical formation of organic aerosols were likely significant over the SCS and EIO, as C<sub>9</sub> diacid is a photochemical oxidation product of unsaturated fatty acids emitted from productive marine regions (Bikkina et al., 2014; Hoque et al., 2017). In addition, the photochemical oxidation of C<sub>9</sub> diacid leads to the generation of its lower homologues including C<sub>4</sub>–C<sub>6</sub> diacids (Yang et al., 2008; Kawamura et al., 1996a). Thus, the similar abundance of diacids (C2-C6 and  $C_9$ ) in the SCS and at Malacca (Fig. 3) suggests that marine biogenic emission was a major source, although the influence of the continental air masses transported from East and Southeast Asia was also significant. However, the concentrations of diacids over Malacca were relatively low, which indicated that the influence of polluted air masses transported from Southeast Asia was lower than that from air masses from East Asia. In general, the abundance of diacids in the EIO-SL and EIO-WI regions was lower than that in the SCS and Malacca regions. This was likely because the air masses that arrived over the EIO-SL and EIO-WI regions mostly originated from remote oceanic regions; thus, marine biogenic emission should have been the major potential source of organic aerosols and the Asian outflow should not have had a significant influence. Interestingly, the concentrations of C<sub>9</sub> diacid (mean of  $68.9 \pm 65.1 \text{ ng m}^{-3}$ ) in the SLDP samples were several times higher than that observed in other regions over the SCS and EIO. As noted above, C<sub>9</sub> diacid is mostly derived from unsaturated fatty acids of biogenic origin and has been considered as a marker for biogenic organic aerosols (Kawamura and Gagosian, 1987). Therefore, the high concentration of C<sub>9</sub> diacid at the SLDP is likely derived from the oxidation of unsaturated fatty acids from mainland biota (Zhao et al., 2018). In fact, terrestrial air masses, which are enriched with higher plant emissions and secondary organic aerosol (SOA) produced upon subsequent oxidation of BVOCs during daytime, are likely transported onshore by land breezes during night-time (Kang et al., 2017). In addition, the photochemical breakdown of C<sub>9</sub> diacid should be insignificant during the night-time hours.

Figure 3 shows the temporal variations in selected diacids over the SCS and EIO during the sampling periods. The spatial patterns of C<sub>6</sub> and C<sub>9</sub> diacids were similar (Fig. 3). C<sub>6</sub> diacid could be produced via the oxidation of cyclic olefins emitted from anthropogenic sources (e.g. fossil fuel combustion; Kawamura et al., 1996a), and it could also be derived from photochemical breakdown of biogenic C<sub>9</sub> diacid (Kawamura et al., 1996b). Bikkina et al. (2015) concluded that the high mass concentrations of C<sub>9</sub> in marine aerosols were consistent with the high biological activity at the ocean surface. This similar temporal variation in C<sub>6</sub> and C<sub>9</sub> diacids and the results of backward trajectories (Fig. 1b) indicate that the formation of C<sub>6</sub> diacid is mostly from the photochemical breakdown of C<sub>9</sub> diacid, which was likely derived from



**Figure 3.** Daily variations in the concentrations of selected organic acids and water-soluble organic carbon (WSOC) in TSP aerosol in the South China Sea and the eastern Indian Ocean from 10 March to 26 April 2015; all parameters are in nanograms per cubic metre (ng m<sup>-3</sup>) except for WSOC, which is in micrograms per cubic metre ( $\mu$ g m<sup>-3</sup>) and chlorophyll *a*, which is in milligrams per cubic metre (mg m<sup>-3</sup>).

marine biogenic emissions. Based on the ultraviolet (UV) irradiation of oleic acid and the ozone system, Matsunaga et al. (1999) found a series of  $C_2$ – $C_9$  diacids, with high abundance of  $C_9$  diacid. Temporal variations in  $C_9$ ,  $C_6$ , and  $C_2$ –  $C_4$  diacids were also similar (Fig. 3), suggesting that the photochemical breakdown of  $C_9$  might be the major formation pathway of short-chain diacids such as  $C_6$ ,  $C_5$ , and  $C_4$ diacids. Further ageing processes eventually led to the formation of  $C_2$  diacid in the EIO. Thus, the molecular distributions and temporal variations of diacids inferred that the organic aerosols collected over the EIO were likely primarily derived from marine biogenic emissions. However, the contribution of diacids to WSOC was reduced in the EIO-WI and EIO-SL due to low biological activity in these oceanic regions, as reflected by the low  $C_9$  diacid loading.

Phthalic acid (Ph acid) is a tracer for anthropogenic organic aerosols. Concentrations of Ph acid in the EIO-WI and EIO-SL were similar to those in western North Pacific aerosol (more biologically influenced aerosols were  $0.6 \text{ ng m}^{-3}$  and less biologically influenced aerosols were  $0.5 \text{ ng m}^{-3}$ ; Bikkina et al., 2015). In addition, concentrations of Ph acid from the SCS to the EIO were much lower than those reported in the urban atmosphere, such as in Chennai (21 ng m<sup>-3</sup>; Pavuluri et al., 2010) and Chinese cities  $(90 \text{ ng m}^{-3}; \text{Ho et al.}, 2007)$ . Ph acid can be released directly from fossil fuel combustion (Kawamura and Kaplan, 1987). Secondary formation via the atmospheric oxidation of aromatic hydrocarbons such as naphthalene is also important (Fu et al., 2009; Ho et al., 2010). Such low levels of Ph acid suggested that the marine aerosols from the EIO were not as seriously impacted by continental air masses from East and Southeast Asia. It is worth noting that Ph was severalfold more abundant at the SLDP than in other regions (Table 1); therefore, we do not preclude the influence of anthropogenic emissions, particularly fossil fuel combustion, associated with the terrestrial air masses that arrived at the SLDP.

#### 3.2.2 Oxocarboxylic acids

Oxocarboxylic acids ( $\omega C_2 - \omega C_9$  and pyruvic acid), the intermediate products of the oxidation of monocarboxylic acids, can be further oxidized to form diacids (Warneck, 2003; Carlton et al., 2007). Similar to diacids, oxocarboxylic acids are mainly derived from combustion sources, but they can also be produced by the photooxidation of various organic precursors from anthropogenic and biological sources in the atmosphere (Kawamura and Bikkina, 2016). The concentrations of total oxoacids ranged from 1.48 to  $13.2 \text{ ng m}^{-3}$ (mean of  $6.51 \pm 3.99$  ng m<sup>-3</sup>) in the SCS, from 0.16 to  $2.01 \text{ ng m}^{-3}$  (mean of  $0.96 \pm 0.46 \text{ ng m}^{-3}$ ) in the EIO-WI, from 0.23 to  $5.06 \text{ ng m}^{-3}$  (mean of  $1.85 \pm 1.51 \text{ ng m}^{-3}$ ) in the EIO-SL, from 0.29 to  $10.4 \,\mathrm{ng}\,\mathrm{m}^{-3}$  (mean of  $4.22 \pm$  $3.75 \text{ ng m}^{-3}$ ) in Malacca, and from 7.46 to  $40.3 \text{ ng m}^{-3}$ (mean of  $24.0\pm16.4$  ng m<sup>-3</sup>) at the SLDP. Thus, the concentrations of total oxoacids in this study were lower than those from Gosan, Jeju Island, South Korea (mean of 53 ng m<sup>-3</sup>; Kawamura et al., 2004) and urban sites in China (45 ng m<sup>-3</sup>; Ho et al., 2007). The concentrations of oxoacids were also lower in the EIO-WI than in the other regions (Table 1). The spatial distributions of  $\omega$ -oxoacids showed the following order with respect to location: SLDP > SCS > Malacca > EIO-SL > EIO-WI. This is consistent with those of major diacids (C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>) and indicates that these oxoacids are potential precursors of dicarboxylic acids (Sempéré and Kawamura, 1994).

Glyoxylic acid ( $\omega$ C<sub>2</sub>) was the most abundant oxoacid followed by pyruvic (Pyr) acid (Table 1). These components are all important intermediates in photooxidation processes and are used in the production of low-carbon-number diacids such as C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub> diacids (Hatakeyama et al., 1987). Several studies have reported that Pyr is produced by the incloud oxidation of isoprene in the atmosphere (Carlton et al., 2006, 2009) which can be transported from mainland regions and/or emitted from the ocean surface (Shaw et al., 2010).

#### 3.2.3 α-Dicarbonyls

The concentrations of total  $\alpha$ -dicarbonyls (glyoxal and methylglyoxal) varied over a wide range  $(0.56-20.2 \text{ ng m}^{-3})$ with a relatively high abundance in the SCS (mean of  $5.25 \pm 4.46 \text{ ng m}^{-3}$ ) and SLDP (mean of  $7.35 \pm 3.58 \text{ ng m}^{-3}$ ). The average concentration of total  $\alpha$ -dicarbonyls during the cruise was higher than those in super-micrometre and submicrometre aerosols collected over the North Pacific in summer  $(0.51 \pm 0.22 \text{ ng m}^{-3} \text{ in more biologically influenced})$ aerosols and  $0.66 \pm 0.20$  ng m<sup>-3</sup> in less biologically influenced aerosols; Miyazaki et al., 2010). The abundances of  $\alpha$ dicarbonyls were higher in the SCS and Malacca than in the EIO-SL and EIO-WI, which were similar to the spacial patterns of diacids and oxoacids (Fig. 2, Table 1). The concentrations of both glyoxal (Gly) and methylglyoxal (MeGly) were higher in the SCS, and their spatial distributions were consistent with those of diacids. Gly and MeGly can be formed via the atmospheric oxidation of isoprene, which is emitted from terrestrial vegetation and/or marine phytoplankton (Sorooshian et al., 2009). In addition, Gly is also a photochemical oxidation product of aromatic hydrocarbons from the combustion of fossil fuels (Carlton et al., 2007; Volkamer et al., 2007). Both species can exist in the aerosol phase and be further oxidized to form less-volatile organic acids such as Pyr,  $\omega C_2$ , and  $C_2$  (Sorooshian et al., 2006). Therefore, the higher abundances of Gly and MeGly over the SCS compared with the other three regions could have been due to enhanced continental outflow as well as the high biological activity at the sea surface. The spatial distributions of total oxoacids and  $\alpha$ -dicarbonyls were similar to those of total diacids, indicating that they had similar origins or formation mechanisms (Kunwar et al., 2017). Based on the backward trajectory analysis, we identified four source regions for diacids and related compounds: (a) East Asia, (b) Southeast Asia, (c) the Bay of Bengal, and (d) the eastern Indian Ocean. When air masses originated from East Asia and Southeast Asia and their coastal areas (i.e. SCS and Malacca), the concentrations of these compounds were high; when air masses were mainly derived from the eastern Indian Ocean (i.e. EIO-WI), their concentrations was the lowest; and when the air masses originated from the Bay of Bengal and the eastern Indian Ocean (i.e. EIO-SL), the concentration of these compounds was between the former two.

# 3.2.4 Fractions of diacids and related compounds in WSOC and OC

Spatial-temporal distributions of WSOC showed much higher values in the SCS and Malacca than in the EIO-WI and EIO-SL regions (Fig. 3j). As discussed above, such a high abundance of WSOC in the SCS and Malacca may have been caused by the enhanced ageing of organic compounds from the surface ocean due to high biological activity and subsequent oxidation that produces more water-soluble organics. In this study, the spatial-temporal trends of diacids and related compounds are generally consistent with those of OC, EC, and WSOC, which are high in the SCS and low in other regions. The fractions of some major diacids, oxoacids, and  $\alpha$ -dicarbonyls in WSOC and OC are presented in Table 2. The total diacids account for  $12.0 \pm 5.75$  % (range of 2.00 %-32.4 %) of WSOC over the EIO, whereas the fractions of oxoacids and  $\alpha$ -dicarbonyls in WSOC ranged from 0.03 % to 1.22 % (mean of 0.34  $\pm$  0.20 %) and from 0.02 % to 3.12% (mean of  $0.60\pm0.68\%$ ) respectively. In addition, a strong linear correlation was found between WSOC and  $C_2$ diacid (Table 2), which suggests that the WSOC was mainly generated via secondary formation rather than via biomass burning emissions associated with the Asian outflow.

## 3.3 Relative abundances of diacids and related compounds

The concentrations of diacids and related compounds and their relative abundances in the atmosphere are controlled by the emission of their precursors and subsequent oxidation processes. Pie diagrams of the percentage contributions of individual straight-chain diacids to total aliphatic diacids in the different regions from the SCS to EIO (SCS, EIO-WI, EIO-SL, Malacca, and SLDP) are depicted in Fig. 4. The percentage contributions of low-molecular-weight diacids, C2-C4, to total mass concentrations,  $\Sigma(C_2-C_{12})$ , varied from 96.4 % to 98.9 % (mean of 97.6  $\pm$  1.25 %) in the SCS, from 85.2 % to 96.0% (mean of  $90.6 \pm 5.38\%$ ) in the EIO-WI, from 90.6 % to 99.4 % (mean of  $95.0 \pm 4.44$  %) in the EIO-SL, from 94.2 % to 98.0 % (mean of 96.1  $\pm$  1.88 %) in Malacca, and from 72.0% to 95.0% (mean of  $83.5 \pm 11.5$ %) at the SLDP. Interestingly, the relative abundances of C<sub>2</sub> to the total mass concentrations of  $C_2$ - $C_{12}$  diacids,  $\Sigma C_2$ - $C_{12}$ , were similar in four regions (Fig. 4). A significant difference was found in the relative abundance of  $C_2$  diacid between SLDP and the other four regions with the lowest value found at the SLDP, whereas  $C_9$  diacid showed the opposite behaviour.

Figure 5 presents the relative abundances of the sums of short-chain diacids  $(C_2-C_4)$ , long-chain diacids  $(C_5-C_4)$ C<sub>12</sub>), unsaturated diacids (M, F, mM, Ph, iPh, and tPh), diacids containing an additional functional group (hC<sub>4</sub>, kC<sub>3</sub>, and kC<sub>7</sub>), oxoacids ( $\omega$ C<sub>2</sub>- $\omega$ C<sub>9</sub> and Pyr), and  $\alpha$ -dicarbonyls (MeGly and Gly) in the measured total diacids and related compounds in different regions from the SCS to EIO. The relative abundances of short-chain diacids were much higher, accounting for about 90% of the total in the SCS and about 60 % in the EIO-WI. Long-chain diacids were found to be second highest at the SLDP and Malacca with respect to abundance, whereas  $\alpha$ -dicarbonyls were second highest in the EIO-WI and EIO-SL; the highest abundances of longchain diacids and  $\alpha$ -dicarbonyls were observed at the SLDP and in the EIO-SL respectively (Fig. 5). Furthermore, the abundance of long-chain diacids was relatively high in the EIO-WI and EIO-SL but was the lowest in the SCS. The relative abundances of unsaturated diacids were the highest in the EIO-WI followed by SLDP, whereas oxoacids were highest in SLDP, followed by the EIO-WI, and showed the lowest values in the SCS and Malacca (Fig. 5). The high abundances of short-chain diacids indicate that the aerosols from the SCS to EIO were significantly aged during long-range transport, while the high abundances of long-chain diacids and  $\alpha$ -dicarbonyls suggest that the contributions from biogenic emissions were much higher over the EIO and at SLDP. The high atmospheric levels of unsaturated fatty acids and oxoacids at the SLDP infer that the contributions from anthropogenic sources are also significant at this location.

# 3.4 Implications for the origins and formation pathways of diacids and related compounds

Different emission sources and the extent of ageing lead to large differences in the concentrations of diacids and related compounds; hence, the mass concentration ratios of selected species can serve as effective markers for the identification of their origins and formation/transformation processes. Temporal variations in the mass ratios of several organic acids as well as the relative abundance of C<sub>2</sub> to total aliphatic diacids are depicted in Fig. 6. The spatial distributions of  $C_3/C_4$ ,  $C_2/C_4$ , and  $C_2/(\Sigma C_2 - C_{12})$  ratios are similar to each other. It has been reported that C<sub>3</sub> diacid can be produced from C<sub>4</sub> diacid by oxidative reaction (Kawamura and Ikushima, 1993). There were robust relationships among  $C_2$ ,  $C_3$ , and C<sub>4</sub> diacids in SCS, EIO-WI, and EIO-SL regions and between C<sub>3</sub> and C<sub>4</sub> diacids in Malacca (Table S1 in the Supplement), suggesting that they were likely derived from similar sources. The C3/C4 ratio can be used as an effective marker to assess the extent of organic aerosol ageing (Kawamura and Ikushima, 1993). The C<sub>3</sub>/C<sub>4</sub> ratios were reported to be low (0.25-0.44) in vehicular emissions, because the C<sub>3</sub>



Figure 4. Pie charts showing the percentage contribution of individual diacids to the total aliphatic homologous diacids ( $\Sigma C_2 - C_{12}$ ) in aerosol from different sea areas collected during the NORC2015-10 cruise.

Table 2. The fractions of diacids and related compounds in WSOC and OC in marine aerosols collected during the NORC2015-10 cruise.

Components	Relative abundance (%)				
	in WSOC	in OC			
Oxalic, C <sub>2</sub>	$0.61 - 14.3 \ (4.78 \pm 2.63)$	$0.28-12.2 (3.52 \pm 2.34)$			
Malonic, C <sub>3</sub>	$0.14 – 2.82 \ (0.85 \pm 0.54)$	$0.07 - 2.41 \ (0.63 \pm 0.50)$			
Succinic, C <sub>4</sub>	$0.10 - 1.94 \ (0.54 \pm 0.37)$	$0.04 - 1.86 \ (0.41 \pm 0.34)$			
$\sum C_2 - C_4$	$1.02-22.0$ (7.50 $\pm$ 4.01)	$0.47 - 18.8 (5.55 \pm 3.68)$			
$\sum$ Diacids	$2.00-32.4~(12.0\pm5.75)$	$0.92-27.7~(8.84\pm5.61)$			
$\sum$ Oxocarboxylic acids	$0.03 - 1.22 \ (0.34 \pm 0.20)$	$0.01 - 1.93 \ (0.26 \pm 0.26)$			
$\sum \alpha$ -Dicarbonyls	$0.02 - 3.12 \ (0.60 \pm 0.68)$	$0.02 - 8.95 \ (0.47 \pm 1.08)$			

diacid is too thermally unstable to be easily degraded during combustion (Kawamura and Kaplan, 1987). In contrast, the  $C_3/C_4$  ratios were reported to be high (range of 1.0–11 and a mean of 3.9) in marine aerosols collected from the North Pacific (including the tropics), which were considered to be photochemically aged during atmospheric transport (Kawamura and Sakaguchi, 1999). The  $C_3/C_4$  ratios in this study ranged from 0.3 to 4.6 with a mean value of 2.0. They are higher than those in urban aerosols from Chinese megacities (range of 0.6–1.1 and mean of 0.74; Ho et al., 2007), Tokyo (range of 0.56–2.9 and mean of 1.6; Kawamura and Ikushima, 1993), and New Delhi, India (range of 0.40–1.1 and mean of 0.66 at daytime and 0.58 at night-time; Miyazaki et al., 2009). It is worth noting that both malonic and succinic acids show a net loss from coastal areas to the open oceans, but the net loss is less for  $C_3$  diacid – which is potentially owing to photochemical processing (Fu et al., 2013a). Therefore, these higher  $C_3/C_4$  ratios suggest that organic aerosols from the SCS to EIO are subjected to significant, intensive photochemical ageing during atmospheric long-range transport via the outflows from East and Southeast Asia to remote oceanic regions (Fig. 1). Furthermore, the  $C_3/C_4$  ratios increased with the decrease of latitude over the SCS, suggesting that the photochemical transformation of  $C_4$  diacid to  $C_3$ diacid was enhanced at lower latitudes due to the increase in temperature and solar radiation. However, such a trend did



**Figure 5.** Relative abundances of individual compound classes in the total diacids, oxoacids, and  $\alpha$ -dicarbonyls in aerosols from different sampling areas collected during the NORC2015-10 cruise.

not appear during the return voyage, and the  $C_3/C_4$  ratios were much lower than those reported over the North Pacific. In addition, the temporal variations in their concentrations were similar throughout the campaign. These results indicate that their in situ formation from the BVOCs (e.g. isoprene) emitted from marine biota might also be significant.

The  $C_2/C_4$  mass ratios can also be used to assess the extent of organic aerosols' ageing (Sorooshian et al., 2007). In the SCS, the  $C_2/C_4$  ratios (7.6–28.9) showed an increasing trend with the decreasing latitude. The  $C_2/C_4$  ratios in the EIO were higher than those reported in Chinese cities (mean of 7.1; Ho et al., 2007), Sapporo (mean of 3.1; Aggarwal and Kawamura, 2008), and South Korea (mean of 8.6; Kundu et al., 2010b). These results indicate that  $C_2$  could be largely generated by the photochemical degradation of C<sub>4</sub> diacid. Moreover, a significant correlation was found between the relative abundance of  $C_2$  ( $C_2$  %) and the  $C_2/C_4$  mass ratio (Fig. S2c), suggesting the potential formation of C<sub>2</sub> diacid from the photochemical breakdown of C4 diacid. A concurrent trend (Fig. 6c) was also obtained for the increased contribution of C<sub>2</sub> to total aliphatic diacids,  $C_2/\Sigma(C_2 - C_{12})$ , suggesting more photochemical ageing of organic aerosols at low latitudes with stronger solar radiation.

The  $C_2/\Sigma(C_2 - C_{12})$  ratio has also been considered as an indicator of the degree of organic aerosols' ageing during long-range atmospheric transport (Wang et al., 2006). In general, the more the aerosol particles are aged, the higher the  $C_2/\Sigma(C_2 - C_{12})$  ratios (Kawamura and Sakaguchi, 1999). The  $C_2/\Sigma(C_2 - C_{12})$  was higher ( $0.76 \pm 0.06$ ) in the SCS than in the EIO-SL ( $0.74 \pm 0.08$ ) and Malacca ( $0.71 \pm 0.11$ ),

followed by the EIO-WI  $(0.65 \pm 0.11)$  and SLDP  $(0.60 \pm 0.11)$ . The values found in this study were also lower than the value reported in wintertime  $(0.8 \pm 0.04)$  and higher than that reported in summertime  $(0.5 \pm 0.01)$  in Himalayan aerosols (Hegde and Kawamura, 2012). These results indicate that the organic aerosols in the SCS were likely more aged and/or influenced by anthropogenic emissions from East Asia, whereas the ageing of organic aerosols was possibly less intensive and influenced by only marine biogenic emissions in the EIO-WI and Malacca. At the SLDP, the low  $C_2/\Sigma(C_2 - C_{12})$  ratio was likely driven by the local coastal biota and the terrestrial biogenic and anthropogenic emissions as well as the less ageing, particularly at night-time.

Maleic acid (M, cis form) is transformed to fumaric acid (F, trans form) with enhanced photochemical activity; hence, the M/F mass ratio has been considered as a proxy to assess the degree of aerosol ageing (Kawamura and Sakaguchi, 1999). In general, low M/F values reflect that secondary oxidation is an important source. M/F ratios were found to be lower in the EIO-WI (0.07–0.73) than in other regions (0.9– 2.3; Table 3). The mean M/F value was 1.33 in samples collected in the SCS, 0.29 in the EIO-WI, 1.30 in the EIO-SL, 2.08 in Malacca, and 1.77 at the SLDP. They were all lower than those in Xi'an aerosols (summer value of 2.22 and winter value of 2.38), and they were about the same or less than those reported at the Korean Gosan site (spring value of 1.38, summer value of 0.76, autumn value of 1.62, and winter value of 2.21), which were considered to be aged. This indicates that the ageing of organic aerosols was more intensive in the EIO-WI, whereas in Malacca and SLDP, the organic aerosols were less aged and/or influenced by local emissions - thus, the *cis-trans* transformation was weak.

According to the description of the origins of  $C_6$ , Ph, and  $C_9$  in the above sections, the  $C_6/C_9$  and  $Ph/C_9$  ratios could provide insight into the relative strength of biogenic and anthropogenic sources in the given area.  $C_6/C_9$  ratios showed lower values in the EIO (except sample no. 2; Fig. 6f), which can be attributed to the large influence from marine air masses containing fatty acids like oleic acid, a precursor of C<sub>9</sub> diacid (Kawamura and Gagosian, 1987). Temporal variations in the Ph/C<sub>9</sub> ratios from the SCS to EIO are shown in Fig. 6g, with a mean of 2.02 in the SCS, 1.56 in the EIO-WI, 1.22 in the EIO-SL, and 0.90 in Malacca. These values were lower than that (5.71) reported for wintertime Gosan aerosols from South Korea (Kundu et al., 2010a) but higher than the values reported for summertime (1.7) and wintertime (1.78) aerosols in Xi'an, China (Wang et al., 2012) and aerosols in the western Pacific (1.41; Sempéré and Kawamura, 2003). These comparisons suggest significant secondary formation of organic aerosols from anthropogenic precursors (e.g. naphthalene) transported from East and Southeast Asia (Fig. 1). However, C<sub>6</sub> and C<sub>9</sub> diacids showed a positive correlation (R = 0.51, p < 0.0001) among all samples, indicating that C<sub>6</sub> diacid is likely also significantly derived from the photooxidation of BVOCs such as



**Figure 6.** Daily variations in the concentration ratios of (a)  $C_2/C_4$ , (b)  $C_3/C_4$ , (c)  $C_2/\Sigma C_2-C_{12}$ , (d)  $C_2/\omega C_2$ , (e)  $C_6/C_9$ , (f)  $C_6/C_9$ , (g) Ph/C<sub>9</sub>, (h) M/F, (i)  $C_2/Gly$ , and (j)  $C_2/MeGly$  in TSP samples collected during the NORC2015-10 cruise.

Mass ratio			Mean $\pm$ SD		
	SCS	EIO-WI	EIO-SL	Malacca	SLDP
$C_2/C_4$	$16.2 \pm 8.14$	$17.1\pm10.6$	$16.1\pm6.72$	$15.1\pm12.4$	8.28±3.80
$C_3/C_4$	$2.18\pm0.95$	$1.79\pm0.90$	$2.05\pm0.80$	$1.99 \pm 1.14$	$1.23\pm0.63$
$C_2/\omega C_2$	$101\pm69.8$	$146\pm220$	$69.7 \pm 41.2$	$721 \pm 1678$	$48.1\pm5.79$
$C_2/Pyr$	$580 \pm 499$	$70.3\pm63.7$	$193\pm191$	$294\pm254$	$267\pm71.0$
$C_2/\Sigma(C_2 - C_{12})$	$0.80\pm0.05$	$0.76\pm0.07$	$0.78\pm0.07$	$0.76\pm0.11$	$0.65\pm0.12$
$C_3 / \Sigma (C_2 - C_{12})$	$0.12\pm0.04$	$0.09\pm0.02$	$0.11\pm0.03$	$0.12\pm0.05$	$0.09\pm0.02$
$C_4 / \Sigma (C_2 - C_{12})$	$0.06\pm0.02$	$0.06\pm0.03$	$0.06\pm0.04$	$0.08\pm0.06$	$0.09\pm0.03$
$C_6/C_9$	$0.76\pm0.93$	$1.17\pm0.76$	$0.49\pm0.52$	$0.49\pm0.39$	$0.11\pm0.07$
Ph/C <sub>9</sub>	$2.02\pm4.26$	$1.66 \pm 1.33$	$1.22\pm1.19$	$0.90\pm0.21$	$0.34\pm0.34$
M/F	$1.33\pm0.52$	$0.29\pm0.19$	$1.30\pm0.59$	$2.08 \pm 1.72$	$1.77\pm0.17$
C <sub>2</sub> /MeGly	$129 \pm 156$	$11.3\pm10.6$	$57.9 \pm 40.8$	$81.9\pm55.5$	$92.1 \pm 13.1$
$C_2/Gly$	$681 \pm 1466$	$14.6\pm15.2$	$127\pm196$	$295 \pm 184$	$77.4\pm21.2$
Gly/MeGly	$0.86\pm0.67$	$1.02\pm0.45$	$1.43\pm2.31$	$0.31\pm0.12$	$1.24\pm0.32$

Table 3. Diagnostic mass ratios of selected diacids and related compounds in TSP samples collected during the NORC2015-10 cruise.

cyclic olefins. The higher  $Ph/C_9$  ratios found over the SCS compared with other regions (Fig. 6g) again suggest that the contribution from fossil fuel combustion is also significant, which is associated with the continental outflow mainly over the SCS and slightly over the EIO.

The origins of MeGly, Gly, Pyr, and isoprene have been discussed in the above sections. The mass ratios such as  $Pyr/C_2$ ,  $\omega C_2/C_2$ ,  $Gly/C_2$ , and  $MeGly/C_2$  can be used to explore the C<sub>2</sub> formation pathway and/or its origin. Here, all the ratios were found to peak in the EIO-WI and/or EIO-SL regions (Fig. 6), where the clean oceanic air masses arrived at the sampling points (Fig. 1), whereas in the SCS, Malacca, and SLDP, these ratios were insignificant except for  $\omega C_2/C_2$ (Fig. 6). These spatial distributions of the  $Pyr/C_2$ ,  $\omega C_2/C_2$ ,  $Gly/C_2$ , and  $MeGly/C_2$  ratios indicate that the loading of organic aerosols in the EIO-WI and EIO-SL regions was likely influenced by marine biogenic emissions and their subsequent oxidation processes. In addition, there were good correlations among Pyr,  $\omega C_2$ , and MeGly in the SCS and Malacca, whereas the correlations were poor in the samples from EIO-WI and EIO-SL (except for Pyr and MeGly in EIO-WI and  $\omega C_2$  and Pyr in EIO-SL). The results showed that organic aerosols produced by BVOCs (e.g. isoprene) emitted from the ocean surface were more aged in the EIO-WI and EIO-SL than in the SCS and at Malacca, where they were affected by anthropogenic emissions.

Finally, to better understand the enhanced emission of unsaturated fatty acids and BVOCs from the biologically active ocean surface from the SCS to EIO, we present the satellite image of chlorophyll-a loading in the EIO in Fig. 1a. The concentrations of chlorophyll a in the SCS and Malacca were higher than in the other regions studied. Interestingly, high concentrations of diacids and related compounds (Fig. 3) were consistent with high concentrations of chlorophyll a at the marine surface. This consistency indicates that the high abundance of diacids in the SCS and Malacca attributes to the oceanic emissions of BVOCs from areas of high biological activity followed by photooxidation, although the influence of anthropogenic emissions associated with the continental outflow cannot be excluded.

#### 4 Conclusions

The dicarboxylic acids, oxocarboxylic acids, and  $\alpha$ dicarbonyls in marine aerosols collected from the SCS to EIO from 10 March to 26 April 2015 provided new insight into their origins and formation processes in tropical regions. The spatial distribution of diacids showed high concentrations in nearshore regions (the SCS, Malacca, and the SLDP) and relatively low concentrations in remote regions (the EIO-WI and EIO-SL). Their molecular distributions were characterized by the dominance of C<sub>2</sub> diacid. Anthropogenic pollutants under Asian outflow conditions strongly influenced the concentrations of dicarboxylic acids in the SCS and Malacca, whereas oceanic biogenic emissions and subsequent oxidation influenced the distributions the above-mentioned species in the EIO-WI and EIO-SL. A close relationship between the temporal variability of C9, C6, and the total concentration of short-chain diacids  $(C_2-C_4)$  implied that the in situ secondary formation of long-chain diacids (including C3 and  $C_4$ ) and related compounds was significant from the SCS to EIO rather than the photochemical breakdown of higher diacids to their lower homologues (despite significant ageing of the air masses transported from the terrestrial region), due to the enhanced emission of VOCs from marine biota in the region. This finding was also supported by good linear relationships among C<sub>4</sub>, hC<sub>4</sub>, and C<sub>3</sub> diacids. The positive correlations obtained between  $C_2 \%$  and the  $C_2/C_4$  ratios and the negative correlations obtained between  $C_2 \%$  and  $C_3 \%$ as well as  $C_4$  % indicated that the formation of  $C_2$  from  $C_4$ 

diacid via C<sub>3</sub> is significant. Furthermore, the enhanced emissions of biogenic unsaturated fatty acids and VOCs from the ocean surface and subsequent photochemical oxidation controlled the high and low levels of diacids and related compounds measured in the SCS and Malacca and in the EIO-WI and EIO-SL respectively. These results combined with 5 d backward air mass trajectories and the satellite image of chlorophyll a suggest that the emission of BVOCs from the biologically active ocean surface and their subsequent oxidation reactions were more significant over the SCS and Malacca than that over the EIO-WI and EIO-SL regions. Finally, SLDP samples were affected by all of the sources mentioned above. In addition, terrestrial biogenic and anthropogenic emissions might have played a significant role in the loading of diacids and related compounds at the SLDP. Further work on the chemical characterization of the marine organic aerosols at a molecular level using high-solution mass spectrometry (MS), such as Orbitrap and Fourier-transform ion cyclotron resonance MS (FT-ICR-MS), are needed to obtain detailed information on sulfur-containing organics from both biogenic and anthropogenic sources.

*Data availability.* The dataset used in this paper is presented in the tables and figures and is available upon request from the corresponding author (fupingqing@tju.edu.cn).

*Supplement.* The supplement related to this article is available online at: https://doi.org/10.5194/acp-20-6841-2020-supplement.

*Author contributions.* PF designed the research. PF and WH supported the research. Samples were collected by LW. Laboratory analyses were performed by JY and WZ. The paper was written by JY, PF, and CMP with consultation from all co-authors.

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

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