Responses to Reviewer #1

We appreciate the reviewers for their thorough reading and thoughtful comments and suggestions, which greatly improve the quality of the manuscript. We revised the MS accordingly. The point-to-point responses to all the comments are given below in blue.

Reviewer #1 (Formal Review for Author (shown to author)):
This observation-base study presents the data of organic aerosol species from a cruise campaign from the South China Sea to the eastern Indian Ocean. It shows the spatial variations of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in the marine aerosols in the investigated oceanic areas. It also discussed their sources and major influence by the oceanic emissions and long-range transport. It could be accepted for publication in ACP after revision.

Response: We thank the reviewer for the comments and the recommendation.

Major comments:
1. I would suggest the authors to re-organize the manuscript in order the present their findings in a clearer way. In the current version, it was not easy for me to follow and to understand the major findings. Some part(s), e.g. their fraction in water-soluble organic carbon, can be moved above to a part maybe mainly describing the overview of data. If possible, the data of ions as well as organic carbon, elemental carbon may be shown there to let the readers quickly get an overview of the data. The authors should also re-organize the discussions for a better presentation of their results and conclusions. For example, the ratios of C_3/C_4 dicarboxylic acids and their correlations are separated into two different parts, which should be merged. These discussions are highly related.

Response: Following the reviewer's suggestion, we have added the description of OC and EC in the revised MS as a sub-section 3.1. Also, the description of WSOC data has been moved to sub-section 3.1 from the 3.5. In addition, the WSOC data has been given in Table 1. The correlations of C_2, C_3, and C_4, and those of C_2% and C_2/C_4, as well as Pyr, ωC_2, and MeGly, and the relevant description of chlorophyll-a in the original sub-section "3.3.2 Linear correlations" have been combined and placed in original sub-section "3.3.1 Diagnostic mass ratios". The rest of original sub-section "3.3.2 Linear correlations" has been moved to the supporting information.

2. I would suggest the authors to polish their findings. What are the major findings in this observation? What information would they like to bring to the readers?

Response: We have improved the discussion of our results to make our findings such as the origins and formation processes (mainly marine BVOCs and *in-situ* secondary formation) over the SCS-EIO region clear to the readers. Please see the abstract and conclusions in the revised MS.

3. Be very careful to deal with the correlations and ratios, I found they may suggest different/contradictory conclusions in the discussion.

Response: We have carefully interpreted the mass ratios and correlations between selected species in assessing the origins and secondary formation/transformations of diacids and related compounds and discussed in detail, without leaving any contradictory view. Please see the sub-section 3.4 in the revised MS.

3. The authors should pay attention to their citations. In these oceanic areas, there are some other observations on organic aerosols which should be inspirational for the authors when undergoing their discussions.

Response: We have tried our best to make modifications to the original text and have added some discussions in the revision. The revised content is as followed:

"The dominance of C_2 followed by C_3 and C_4 diacids is consistent with those coastal marine aerosols (Kundu et al., 2010;Kunwar and Kawamura, 2014) and remote marine aerosols from the western North Pacific (Bikkina et al., 2015), suggesting similar formation processes of dicarboxylic acids in the atmosphere." (see Page 8, Line 213–216).

We also added the following sentences in the revised manuscript.

"For the aerosol samples of SCS, the 5-day back trajectories (Fig. 1b) showed that the air masses were originated from East Asia, whereas the air masses of Malacca were delivered from Southeast Asia. The concentration of diacids and related compounds were highest in SCS and second highest in Malacca, due to increased anthropogenic activities through long-range atmospheric transport in East Asia and Southeast Asia, respectively." (see Page 8, Line 206–210)

"The spatial distributions of total oxoacids and α-dicarbonyls were similar to those of total diacids, indicating that they were similar in origin or formation mechanism (Kunwar et al., 2017). Based on the backward trajectory analysis, we identified four source regions of diacids and related compounds: (a) East Asia, (b) Southeast Asia, (c) the Bay of Bengal, and (d) the East 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 East Indian Ocean (i.e. EIO-WI), their concentrations was the lowest; and when the air masses originated from the Bay of Bengal and the East Indian Ocean (i.e. EIO-SL), the concentration of these compounds was between the former two." (see Page 12, Line 327–335)

4. Some figures can be moved to the supporting information. For example, Figure 2 only shows the chemical structures of the diacids. It is hard to get information from Figure 9 efficiently. Figure 8 could also be moved to the SI.

Response: In the revision, we have moved Figure 2, Figure 8 and Figure 9 to the supporting information (SI).

5. L301-305: I do not understand why? From the ratios, we could say these aerosol particles are aged but it is hard to know if they are influenced by marine biota or continental anthropogenic emissions.

Response: To avoid such confusion/misunderstanding to the reader, we modified the discussion by removing the following sentence: "Further ---- emissions." and by detailing the interpretations of the ratios and correlations of the selected species. In fact, the air masses transported from the continental regions are aged (confirmed by C_2%) and also mainly influenced by the marine biota emissions (confirmed by the mass ratios and correlations between species, e.g., C_6 and C_9 diacids). We detailed these points in the revised MS (please see sub-section 3.4).

6. L361-365: The sentence is too long and hard to be followed. Please rephrase it.

Response: Now the revised sentences are as follows:

"In addition, there were good correlations among Pyr, ωC_2 and MeGly in the SCS and Malacca, while the correlations were poor in the samples from EIO-WI and EIO-SL (except for Pyr and MeGly in EIO-WI, and ωC_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 the SCS and Malacca where were affected by anthropogenic emissions." (see Page 15, Line 437–441)

7. Line 394-396: I do not see the high Chlorophyall-a concentrations in the SCS in the satellite image (Figure 1a). A close look at a special case of some samples (e.g. 55-60) would be necessary.

Response: The manuscript shows the time series diagram of chlorophyll-a in Figure 3k. It can be seen that the concentration of chlorophyll-a in SCS and Malacca is significantly higher. In addition, the concentration of chlorophyll-a in samples No. 55-60 was also higher. 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). Spatial distributions of marine VOCs 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 stand for higher biological activities and more active to the emission of VOCs (Kang et al., 2018).

8. Minor errors:

L210: it should be “lower than”

Response: We have corrected the mistake in the revised manuscript. “The concentrations of total oxoacids are lower than those from Gosan, Jeju Island, South Korea (average 53 ng m^{-3}) (Kawamura et al., 2004) and urban sites in China (45 ng m^{-3}) (Ho et al., 2007).” (see Page 11, Line 303)

L298-299: should the sentence be “the more the aerosol particles are aged, the higher the ratios are”?

Response: We have corrected the mistake in the revised manuscript. “In general, the more the aerosol particles are aged, the higher the $C_2/\Sigma(C_2–C_{12})$ ratios are (Kawamura and Sakaguchi, 1999).” (see Page 14, Line 398–399)

L311: “attribute for” should be “attribute to”

Response: We have corrected the mistake in the revised manuscript. (see Page 15, Line 419)

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Responses to Reviewer #2

We appreciate the reviewer for the thorough reading and thoughtful comments and suggestions, which greatly improve the quality of the manuscript. We have carefully revised the MS accordingly. The point-to-point responses to all the comments are given below in blue.

Reviewer #2 (Formal Review for Author (shown to author)):
The manuscript studied the distributions of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in marine aerosols during a cruise from 10 March to 26 April 2015. The cruise area is over South China Sea to East Indian Ocean. There were many samples collected, and the analysis were based on four regions, SCS, EIO-WI, EIO-SL, and SLDP. Through the different concentrations and ratios of dicarboxylic acids, oxoacids and α-dicarbonyls, their sources and possible formation pathways in each studied region were discussed. The work in this manuscript is very important. However, the article still needs to be major revised and then can be published on Atmos. Chem. Phys.

Major Comments:
1. The main meaningful was not very clear during the part of Introduction. The author should give more discussion about this cruise especially the important of this studied area in the Introduction.

Response: Thanks for the reviewer's suggestions. We added the following sentences in the revised manuscript in the section of Introduction.

"Land-sea-air interaction is one of the most important issues in earth system science. Atmospheric aerosol is the major component in the Earth's atmosphere and is one of the key carriers of the global biogeochemical cycle of nutrients (Zhuang et al., 1992;Li et al., 2017;Tan et al., 2011)." (see Page 2, Line 35–37)

"The oceans account for 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 matters in the tropical marine atmosphere is very limited." (see Page 3, Line 79–81)

"Studies on the molecular composition and distribution of dicarboxylic acids and related compounds can provide useful information for source analysis, secondary formation and photochemical transformation processes of atmospheric organic aerosols." (see Page 3, Line 97–99)

"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 South China Sea is mainly influenced by the northeast monsoon roughly from mid-October to mid-March of the following year and by the southwest monsoon from mid-May to mid-September; while from mid-March to mid-May is the spring transition period, during which the wind direction is variable. The climate of the South China Sea 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 at the same latitude, so it is called the tropical ocean. The tropical East Indian Ocean (10°S–15°N, 65°E–100°E), including the southern bay of Bengal, southeastern Arabian Sea, 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)." (see Page 3–4, Line 81–93)

2. There are many analyses and data in the manuscript. It is very difficult for readers to understand the information present in the article because of the illogical.

Part 3.1.1 Dicarboxylic acids:

There are many discussions about C_9 in paragraph 4, 5, 6, 7, and discussions about Ph in paragraph 5 and 8. The whole part of 3.1.1 is very illogical, and I can't catch the important point and main results. The author should analysis the main connection between these dicarboxylic acids and different areas, give more clearly analysis. For example, form the analysis in the manuscript, the most important dicarboxylic acid is the C_9 which have relation with C_2–C_4, C_6, and Ph. The author can put these results together and give the discussion, then give the main point of these results.

Response: Thanks for the reviewer's suggestions. The revised manuscript have moved the overall description of dicarboxylic acids and related compounds to the front of Section 3.2.1 (original section 3.1.1), and have reorganized the contents of Section 3.2.1 (original Section 3.1.1) into four paragraphs, i.e. the first paragraph introduces C_2–C_4, the second paragraph introduces C_9, the third paragraph introduces C_6, and the fourth paragraph introduces Ph. The logic of the revised manuscript should be clear enough for reader to follow. And at the beginning of Section 3.2.1, a general sentence has been added:

“C_2–C_4, C_6, C_9 and Ph are important species of dicarboxylic acids; this section briefly summarizes the main sources and/or formation processes of these organic acids.” (see Page 9, Line 238–239)

Part 3.1.2 Oxocarboxylic acids:

The meaning of oxocarboxylic acids in the secondary paragraph should be discussed firstly in this part.

Response: Thanks for the reviewer’s suggestions. At the beginning of Part 3.2.2 (original Part 3.1.2), this manuscript has noted that oxocarboxylic acids mainly contain ωC_2−ωC_9 and pyruvic acid, and have added the following sentence:

“Being similar to diacids, oxocarboxylic acids are mainly derived from combustion sources, but can also be produced by photooxidation of various organic precursors in the atmosphere from anthropogenic and biological sources (Kawamura and Bikkina, 2016).” (see Page 11, Line 297–300)

Part 3.3.1 Diagnostic mass ratios:

The data of C_3/C_4, C_2/C_4, $C_2/\Sigma(C_2-C_{12})$, and M/F can give the information of organic aerosols aging. And they can be put together to give the discussion which can be more clearly.

Response: The revised manuscript has moved the content of M/F in Section 3.4 (original Section 3.3.1), and discussed it with C_3/C_4, C_2/C_4, $C_2/\Sigma(C_2-C_{12})$, to explain the aging of organic aerosols.

Part 3.3.2 Linear correlations:

This part can be put in the supporting information, the authors just give the result when other parts need to be supported. For example, line 443-446.

Response: This manuscript has merged the content of the original “Section 3.3.1 Diagnostic mass ratios” and the original “Section 3.3.2 Linear correlations”, so there is not subtitle in Part 3.3. That is to say, the correlation of C_2, C_3, and C_4, the correlation of C_2% and C_2/C_4, the correlation of Pyr, ωC_2, and MeGly, and the relevant description of chlorophyll a in the original “Section 3.3.2 Linear correlations” has been moved into the “Section 3.3.1 Diagnostic mass ratios”, and the rest of original “Section 3.3.2 Linear correlations” has been moved to the supporting information.

3. The authors just compare their data with references, but the discussions are not enough.

Line 158-159, Line 161-164, Line 220 “Oxoacids showed a predominance of ωC2 or ωC3 in five sampling areas (Fig. 3).” Line 221-224.

Response: Thanks for the reviewer for pointing this deficiency. Regarding original “Line 158-159”, the revised manuscript has added the following discussion after it:

“Therefore, combined with the geographical location of SLDP and the fact that the samples were collected in the ship's docking port, it is speculated that the organic aerosol samples of SLDP may be affected by local coastal and terrestrial biological sources and anthropogenic emissions (especially fossil fuel combustion).” (see Page 8, Line 233–236)

Regarding original “Line 161-164”, the revised manuscript has added the following discussion after it: “It can be clearly seen that the concentrations of C_2 in SCS and Malacca were higher than those in EIO-SL and EIO-WI (Table 1). The large amount of C_2 can be 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), photooxidation of VOCs and other precursors (Kawamura and Yasui, 2005;Kundu et al., 2010). The diurnal variation trend of C_2 was similar to that of C_3 and C_4, indicating that these compounds may have similar photochemical oxidation pathways or emission sources in the atmosphere.” (see Page 9, Line 242–248)

Regarding original “Line 220-224”, the phrase “Oxoacids showed a predominance of ωC_2 or ωC_3 in five sampling areas (Fig. 3)” has been deleted from the revised manuscript because it overlaps with the next paragraph. And, we have added the following discussion after original “Line 221-224”: “The spatial distributions of ω-oxoacids showed a pattern of SLDP > SCS > Malacca > EIO-SL > EIO-WI, being consistent with those of major diacids (C_2, C_3, and C_4), which indicated that these oxoacids were potential precursors of dicarboxylic acids (Sempéré and Kawamura, 1994).” (see Page 11, Line 305–307)

4. There are many repetitions in the article not only the example below.

The sources of C_9 and the relation of C_9 with other carboxylic acids were discussed repeatedly in part 3.1.1.

Part 3.3.1, the meaning of C_6, Ph, MeGly, Gly, Pyr, Isoprene has been given in the former part, delete the repetitions.

Response: We have reorganized the contents of Section 3.2.1 (original Section 3.1.1) and merged them into four paragraphs. That is, the first paragraph introduces C_2–C_4, the second paragraph introduces C_9, the third paragraph introduces C_6, and the fourth paragraph introduces

Ph. The logic of the revised manuscript is clearer. In addition, we have deleted the meanings of C_6, Ph, MeGly, Gly, Pyr and isoprene in Section 3.4 (original Section 3.3.1).

Minor comments:

Line 254 “C_{10}” to “C_{12}”.

Response: Thanks. We have corrected the mistake in the revised manuscript: “Interestingly, the relative abundances of C_2 to total mass concentrations of C_2 to C_{12} diacids (ΣC_2–C_{12}) were similar in four regions (Fig. 5).” (see Page 12, Line 343–344)

Line 386 delete “isoprene and/or aromatic hydrocarbon oxidation products”.

Response: Corrected.

Line 287, “It is worth noting that both C3 and C4 acids show a net loss…”

Response: Thanks. This sentence has been deleted from the revised manuscript because it does not make sense to place it there.

Line 202, delete one “that”.

Response: We have corrected the mistake in the revised manuscript: “Temporal variations in C_9, C_6, and C_2−C_4 diacids were also similar (Fig. 3), suggesting that 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.” (see Page 10, Line 280–282)

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A list of all relevant changes made in the manuscript

1. Extra description of the background of marine organic aerosols in the tropical regions are provided in Section 1 – “Introduction” in the revised manuscript.
2. Detailed information on OC, EC and WSOC are provided in Section 3.1 in the revised manuscript.
3. Some missing introductions and information are added in other parts of Section 3.
4. Supporting Information is provided in the revision. Detailed linear correlation description and three figures (Fig S1 – Fig. S3) are presented and moved from the main text to the Supporting Information.

Molecular and spatial distributions of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in marine aerosols over the South China Sea to East Indian Ocean

Jing Yang[1,2], Wanyu Zhao[2,4], Lianfang Wei[2], Qiang Zhang[1], Yue Zhao[1], Wei Hu[1], Libin Wu[1], Xiaodong Li[1], Chandra Mouli Pavuluri[1], Xiaole Pan[2], Yele Sun[2], Zifa Wang[2], Cong-Qiang Liu[1], Kimitaka Kawamura[3], and Pingqing Fu[1]

[1]Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China
[2]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China
[3]Chubu Institute for Advanced Studies, Chubu University, Kasugai 487-8501, Japan
[4]College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing, 100049, China

Correspondence to: Pingqing Fu (fupingqing@tju.edu.cn)

Abstract. Marine aerosol samples collected from the South China Sea (SCS) to the East Indian Ocean (EIO) during a cruise from March 10 to April 26, 2015 were studied for diacids and related compounds. In view of the air masses backward trajectories and source regions of geographical features, the cruise area was categorized into the South China Sea (SCS), the East Indian Ocean off the coast of western Indonesia (EIO-WI), the EIO off the coast of Sri Lanka (EIO-SL), Malacca and Sri Lanka docking point (SLDP). Total concentrations of diacids, oxoacids and α-dicarbonyls were much higher at SLDP followed by the SCS, Malacca, and the lowest at the EIO-WI. In this study, oxalic acid (C_2) was the dominant diacid during the cruise, followed by malonic acid (C_3) in the SCS, EIO-WI, EIO-SL and Malacca, whereas succinic acid (C_4) diacid was relatively more abundant than C_3 diacid in SLDP. Except for SLDP, C_3/C_4 mass ratios were always greater than 1, and no significant difference was observed among the cruise. The C_2/C_4 and C_2/total diacids ratios also showed the similar trends. Average mass ratios of adipic acid (C_6) to azelaic acid (C_9) were less than unity except for at EIO-WI; the mass ratios of phthalic acid (Ph) to azelaic acid (C_9) were less than 2 except for at SCS. The concentrations of diacids were higher when the air masses originated from the terrestrial regions than those from the remote oceanic regions. Based on the molecular distributions of organic acids, the mass ratios and 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 oxidations was the main contributor to diacids, oxocarboxylic acids and α-dicarbonyls over the SCS to EIO. In addition, the continental outflow that enriched with the anthropogenic VOCs and their aging influenced the organic aerosol loading, particularly over the SCS. The emissions from Sri Lanka terrestrial

vegetations as well as fossil fuel combustion and subsequent photochemical oxidation also played a prominent role in controlling the organic aerosols loading and molecular distributions of diacids and related compounds at SLDP.

1 Introduction

Land-sea-air interaction is one of the most important issues in earth system science. Atmospheric aerosol is the major component in the Earth's atmosphere and is one of the key carriers of the global biogeochemical cycle of nutrients (Zhuang et al., 1992;Li et al., 2017;Tan et al., 2011). Atmospheric aerosol containing inorganic and organic materials plays a vital role in air quality, atmospheric chemistry, health of human and ecosystems, and has a critical impact on the global climate system (Ramanathan et al., 2001). Organic aerosols in tropospheric regions account for up to 90% (Kanakidou et al., 2005), and most of them are water-soluble (Kanakidou et al., 2005). The abundant diacids, oxoacids and α-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), which enhance the capacity of aerosol particles to act as cloud condensation nuclei and ice nuclei in the atmosphere (Ervens et al., 2011;Zhao et al., 2016a;Vergara-Temprado et al., 2017;Huang et al., 2018), whereas the water-insoluble substances such as lipid class compounds can reduce their hygroscopic activity (Kawamura et al., 2017).

It has been well established that the aerosols in the marine atmosphere are influenced by the emissions from the ocean surface, such as plankton activities (Cavalli et al., 2004;O'Dowd and De Leeuw, 2007;Facchini et al., 2008). Marine emissions account for more than half of the global natural aerosol burden (1000–3000 Tg yr^{-1}) (Iii and Duce, 1988), and thus significantly influence the Earth's climate system (Haywood and M., 1999). Previous studies on marine aerosols have focused mainly on the measurements of non-sea-salt/sea-salt sulfates (Charlson et al., 1987;Charlson et al., 1992) and mineral dust (Schulz et al., 2012). However, diacids and related compounds in marine aerosols have been paid little attention to, despite the fact that they account for >10% of total carbon (TC) in the 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 formed by atmospheric oxidation of various volatile organic compounds (VOCs) emitted from primary sources (Kawamura et al., 1996a). In addition, unsaturated fatty acids emitted from the 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 (C_2–C_4) (Nguyen et al., 2010).

Chemical characterization of dicarboxylic acids, oxoacids and α-dicarbonyls in atmospheric aerosols provides useful knowledge on the relative contribution of possible primary sources, the long-range atmospheric transport and the photo-oxidation routes of organic compounds (Kawamura and Bikkina, 2016). Many studies have investigated the impacts of the continental air outflows on the concentrations, compositions and distributions of organic aerosols in the marine areas (Fu et al., 2013a). For example, a long-term observation of aerosols at the Chichi-jima 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 by the westerlies (Mochida et al., 2003a). Moreover, organic compounds from marine sources, such as unsaturated fatty acids, 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 activities in the North Pacific Ocean. Meanwhile, the oxidation products (e.g. pyruvic and glyoxylic acids) of isoprene observed in the marine boundary layer had a similar concentration trend with that of C_2, suggesting that the secondary oxidation of biogenic VOCs from marine sources significantly contribute to the atmospheric loading of diacids and related compounds.

The oceans account for 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 matters 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 South China Sea is mainly influenced by the northeast monsoon roughly from mid-October to mid-March of the following year and by the southwest monsoon from mid-May to mid-September; while from mid-March to mid-May is the spring transition period, during which the wind direction is variable. The climate of the South China Sea 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 at the same latitude, so it is called the tropical ocean. The tropical East Indian Ocean (10°S–15°N, 65°E–100°E), including the southern bay of Bengal, southeastern Arabian Sea, 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 research field of atmospheric organic aerosols, the studies on diacids, oxoacids and α-dicarbonyls in the marine atmosphere are scarce and limited to the Mediterranean, North Pacific, South Pacific, Caribbean and Atlantic Ocean (Kawamura and Bikkina, 2016), while little is known about the 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, secondary formation and photochemical transformation processes of atmospheric organic aerosols. In this study, total suspended particle (TSP) samples collected on day- and night-time basis over the South China Sea and the East Indian Ocean were studied for diacids, oxoacids, and α-dicarbonyls, which provided an ideal opportunity to investigate the spatial distributions of marine organic aerosols which influenced by organics from both marine emissions and long-range transported continental aerosols. In addition, carbonaceous components, i.e. organic (OC) and elemental carbon (EC) and water-soluble OC (WSOC) in the TSP samples were measured. Based on the molecular and spatial distributions, and mass ratios of organic compounds and relations with bulk components together with the backward air mass trajectories, we discuss their sources and possible formation pathways in the studied region.

2 Materials and methods

2.1 Marine aerosol sampling

Marine aerosol sampling was performed on the *R/V* "Shiyan 1" during the cruise NORC2015-10 in the South China Sea and the East Indian Ocean (Figure 1) from 10 March to 26 April 2015. TSP samples were collected on daytime (n = 44) and nighttime (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 the potential pollution from the ship emissions. The three samples collected at the Sri Lanka docking point (SLDP) when the ship was docked in the port, which were seriously polluted by ship exhaust emission. Therefore, these three samples were discussed separately to compare with other samples. The air sampler was operated at a flow rate of 1.0 m^3 min^{-1} with pre-combusted (450°C, 6h) quartz filters (25 cm × 20 cm, PALLFLEX®TM, 2500 QAT-UP). We also collected field blanks (n = 4) during the cruise. After sampling, the filter samples were wrapped in aluminum foil and packed in zip-lock bag and stored in dark at –20°C until the chemical analysis.

Five-day air mass backward trajectories arriving at 100 m above the sea level on each day were computed using the HYSPLIT model (https://www.ready.noaa.gov/HYSPLIT.php) (Figure 1). The air masses arriving over the South China Sea (SCS) originated from East Asia and surrounding oceanic regions. Those arrived over the East Indian Ocean off the coast of western Indonesia (EIO-WI) originated from the remote EIO, while those arriving over the EIO off the coast of Sri Lanka (EIO-SL) were mixed from the remote EIO and Bay of Bengal. The air masses arrived over Malacca from the Southeast Asian subcontinent and the surrounding EIO. In addition, the vessel was docked for 3 days at Sri Lanka docking point (SLDP), during which the air masses were originated from the surrounding oceanic regions. Thus, the TSP samples collected in these different locales during the cruise may have been affected by the long-distance atmospheric transport, and hence we segregated the TSP samples into five categories: SCS, EIO-WI, EIO-SL, SLDP and Malacca (Figure 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 with organic-free Milli-Q water (10 mL) under ultrasonication for three times. Then, the extracts were concentrated to dryness and reacted with 14% BF_3/*n*-butanol at 100°C for 1 hour. The derivatized acids and carbonyls were extracted with *n*-hexane and injected into a split/splitless gas chromatography (GC-FID, Agilent 6980) equipped with an HP-5 column for the determination of diacids and related compounds. The field blank filters were also analyzed using the same experiment procedure. Recoveries of major organic acids were better than 85%. The analytical errors in 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 cm^2 or 34.7 cm^2 of each filter was extracted with Milli-Q water (20 mL) under ultrasonication for 20 min. The extracts were analyzed using a total organic carbon (TOC) analyzer (TOC-L, 5000A, Shimadzu, Japan) for WSOC. OC and EC were determined using a carbon analyzer (Sunset Laboratory Inc., USA) using a piece (1.5 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 μgC cm^{-2} with a precision of >10%. Concentrations of all 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 concentrations of EC (4.24±3.02 μg m^{-3}) in SLDP aerosols were much higher than those in other regions (SCS: 0.27±0.15 μg m^{-3}; EIO-WI: 0.05±0.05 μg m^{-3}; EIO-SL: 0.04±0.18 μg m^{-3}; and Malacca: 0.24±0.18 μg m^{-3}), which proved that the samples of SLDP were seriously polluted by ship exhaust, but other sea areas should be minor.

3 Results and discussion

3.1 OC, EC and WSOC in marine aerosols

The concentrations of OC, EC and WSOC in each marine region (SCS, EIO-WI, EIO-SL, SLDP and Malacca) are summarized in Table 1. In the TSP samples collected in the South China Sea to the East Indian Ocean from March to April 2015, the mass concentration of OC and EC varied from 0.02 to 20.9 μg m^{-3} (average 1.29±2.72 μg m^{-3}) and from 0.00 to 7.57 μg m^{-3} (average 0.33±0.90 μg m^{-3}), respectively. Generally, the mass concentrations of OC and EC in SLDP were the highest, followed by Malacca and SCS, and the lowest in EIO-WI and EIO-SL. In this study, the mean mass concentrations of OC and EC in SCS were 1.5 times (OC: 0.82 μg m^{-3}) and 1.7 times (EC: 0.16 μg m^{-3}) higher than those reported by Fu et al. (2013a) in the South China Sea in late February 1990. Because of the same sampling season, the above situation indicated that with the economic development of the surrounding areas of the South China Sea, the input of anthropogenic emissions to the South China Sea carbon aerosols were also increasing. In this study, the concentrations of carbon components in SCS and Malacca were similar to those reported in Okinawa Island (OC: 1.78 μg m^{-3}, EC: 0.28 μg m^{-3}) (Kunwar and Kawamura, 2014a). The concentration of carbon components in SLDP was relatively close to that of Jeju Island (OC: 11.3 μg m^{-3}, EC: 3.0 μg m^{-3}) (Jung and Kawamura, 2011), and was higher than that of Sapporo, Hokkaido (OC: 6.1 μg m^{-3}, EC: 1.9 μg m^{-3}) (Simoneit et al., 2004), these two sites were greatly affected by terrestrial long-distance transmission. Meanwhile, the concentrations of carbon components in EIO-WI and EIO-SL were lower than those in Northern Atlantic (OC: 0.93 μg m^{-3}, EC: 0.27 μg m^{-3}) (Zhang et al., 2010), Pacific (OC: 0.82 μg m^{-3}, EC: 0.22 μg m^{-3}) (Zhang et al., 2010), Amsterdam Island (OC: 0.24 μg m^{-3}, EC: n.d.) (Claeys et al., 2010), Arctic ocean (OC:0.56 μg m^{-3}) (Fu et al., 2013b) and so on. These places were all less affected by terrestrial anthropogenic emissions.

EC is the product of residential coal, fossil fuel combustion and incomplete combustion of biomass, while OC contains both primary organic carbon and secondary organic aerosol generated by photochemical reactions of organic gases in the atmosphere. The concentration of EC in SLDP aerosol (4.24±3.02 μg m^{-3}) was much higher than that in other marine areas (SCS: 0.27±0.15 μg m^{-3}, EIO-WI: 0.05±0.05 μg m^{-3}, EIO-SL: 0.21±0.18 μg m^{-3}, Malacca: 0.24±0.18 μg m^{-3}), indicating that the aerosol samples of SLDP were seriously polluted by ship exhaust but not for the other marine samples. OC and EC can roughly determine the source of the aerosols. There was a weak correlation between the concentration of OC and EC in aerosols from the South China Sea to the East Indian Ocean (R^2=0.34, P<0.001), indicating that the origins of organic aerosols were different from that 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 was greater than 2, it indicates the presence of secondary organic aerosols. The OC/EC ratio was 5.52±5.33 (range 1.02–29.7) in SCS, 11.84±17.44 (range 1.55–51.0) in EIO-WI, 0.96±2.33 (range 0.96–9.28) in EIO-SL, 8.76±6.84 (range 2.71–24.4) in Malacca, and 2.98±0.97 (range 2.14–4.04) in SLDP. Among them, the ratio of OC/EC in SCS was very similar to that measured by Fu et al. (Fu et al., 2013a) in TSP samples collected in the South China Sea (OC/EC: 5.1). The above results indicated that the contribution of secondary organic aerosols was widespread in aerosol samples from the South China Sea to the East Indian Ocean, except for some samples in EIO-WI and EIO-SL.

The concentrations of water-soluble organic carbon (WSOC) were higher (range 1.12–7.44 ng m^{-3}, average 4.43 ± 3.17 ng m^{-3}) in the SLDP followed by Malacca (0.09–2.72 ng m^{-3}, 1.15±0.92 ng m^{-3}), SCS (0.22–2.31 ng m^{-3}, 1.05 ± 0.65 ng m^{-3}), EIO-SL (0.06–1.00 ng m^{-3}, 0.35 ± 0.25 ng m^{-3}) and EIO-WI (0.05–0.58 ng m^{-3}, 0.15±0.12 ng m^{-3}). The WSOC concentrations over the SCS to EIO are much lower than those in urban aerosols from Tokyo (average 13 μg m^{-3}) (Sempére and Kawamura, 1994) and in the biomass burning aerosols from Amazonia (18–51 μg 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 (average 0.30 μg m^{-3}) (Hoque and Kawamura, 2016), the western Pacific (average 0.33 μg m^{-3}) (Sempéré and Kawamura, 2003), and Hawaii (average 0.39 μg m^{-3}) (Hoffman and Duce, 2013). Kawamura et al. (2010) determined lower WSOC concentrations (0.04–0.30 μg m^{-3}, average 0.18 μg m^{-3}) in the 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 α-dicarbonyls in each marine region (SCS, EIO-WI, EIO-SL, SLDP and Malacca) are summarized in Table 1. Their chemical structures are shown in Fig. S1. Most of the organic species were found to be more abundant at SLDP followed by the SCS, Malacca, EIO-WI and EIO-

SL, respectively (Table 1). For the aerosol samples of SCS, the 5-day back trajectories (Fig. 1b) showed that the air masses were originated from East Asia, whereas the air masses of Malacca were delivered from Southeast Asia. The concentrations of diacids and related compounds were the highest in SCS followed by Malacca, due to increased anthropogenic activities through long-range atmospheric transport in East Asia (Zhao et al., 2016b) and Southeast Asia, respectively. C_2 diacid showed the highest abundance followed by $C_3 > C_4 >$ MeGly $> \omega C_2 > C_5 >$ Ph $\approx$ Gly $> C_9$ (see Table 1 for full form of abbreviation) among the measured major species over the SCS (Fig. 2a), while $C_3 >$ MeGly $> C_4 >$ F $>$ Ph $> C_6 \approx C_9$ over the EIO-WI (Fig. 2b), $C_3 > C_4 > C_9 \approx$ MeGly $> \omega C_2 >$ Gly $>$ Ph at EIO-SL. The order in Malacca was $C_2 > C_3 > C_4 > kC_7 > C_5 > \omega C_2 > C_9 \approx$ MeGly. The dominance of C_2 followed by C_3 and C_4 diacids is consistent with those coastal marine aerosols (Kundu et al., 2010b;Kunwar and Kawamura, 2014b) and remote marine aerosols from the western North Pacific (Bikkina et al., 2015), suggesting similar formation processes of dicarboxylic acids in the atmosphere.

Total concentrations of diacids over Malacca varied from 21.9 to 501 ng m^{-3} (average 207±158 ng m^{-3}) and the SCS from 44.6 to 759 ng m^{-3} (305±186 ng m^{-3}), which were similar to those reported over the East China Sea (325 ng m^{-3}) and Indian Ocean (301 ng m^{-3}) during a round-the-world cruise (Fu et al., 2013a). The average concentration of diacids over the EIO-SL (77.6±73.1 ng m^{-3}) was similar with those over the western North Pacific (87 ng m^{-3} in more biologically influenced aerosols) (Miyazaki et al., 2010) and Atlantic Ocean (95 ng m^{-3}) (Fu et al., 2013a). Total concentrations of diacids over the EIO-WI varied from 8.28 to 96.3 ng m^{-3} (26.1±23.3 ng m^{-3}), which were comparable to those from the western North Pacific (34 ng m^{-3} in LBA) (Miyazaki et al., 2010) and western Pacific Ocean (60±39 ng m^{-3}) (Wang et al., 2006), and were higher than that from the Southern Ocean (4.5±4.0 ng m^{-3}) (Wang et al., 2006). The average concentration of diacids over SLDP (514±231 ng m^{-3}) was lower than those reported from Gosan, Jeju Island, South Korea (660 ng m^{-3} in 2004 and 636 ng m^{-3} in 2010b) (Kawamura et al., 2004;Kundu et al., 2010b), the East China Sea (850 ng m^{-3}) (Mochida et al., 2003b), California coast (424 ng m^{-3}) (Fu et al., 2013a), the urban center of Xi'an, China in different dust events (932–2240 ng m^{-3}) (Wang et al., 2015), the megacity Chennai, India (694.5±176.3 and 640.6±150.6 ng m^{-3} in early and late winter) (Pavuluri et al., 2010), and was comparable to those from the megacity Chennai, India in summer (502.9±117.9 ng m^{-3}) (Pavuluri et al., 2010). However, the concentration of diacids over SLDP was much higher than that from Chichi-jima Island, Japan (139 ng m^{-3}) (Mochida et al., 2003a). Therefore, combined with the geographical location of SLDP and the fact that the samples were collected in the ship's docking port, it is speculated that the organic aerosol samples of SLDP may be affected by local coastal and terrestrial biological sources and anthropogenic emissions (especially fossil fuel combustion). The pattern of diacids abundance order ($C_2 > C_9 > C_4 > C_3 >$ Ph $> C_5$) observed at SLDP was similar to that in continental aerosols (Kawamura and Bikkina, 2016).

3.2.1 Dicarboxylic acids

C_2–C_4, C_6, C_9 and Ph are important species of dicarboxylic acids; this section briefly summarizes the main sources and/or formation processes of these organic acids. C_2 diacid concentrations ranged from 4.43 to 70.1 ng m^{-3} with an average of 18.2 ± 18.4 ng m^{-3} in the EIO-WI, 5.21–232 ng m^{-3} (average 58.2 ± 55.3 ng m^{-3}) in the EIO-SL, 14.5–373 ng m^{-3} (145 ± 112 ng m^{-3}) in Malacca, 30.3–626 ng m^{-3} (233 ± 143 ng m^{-3}) in the SCS and 179–454 ng m^{-3} (303 ± 140 ng m^{-3}) in SLDP. It can be clearly seen that the concentrations of C_2 in SCS and Malacca were higher than those in EIO-SL and EIO-WI (Table 1). The large amount of C_2 can be 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), photooxidation of VOCs and other precursors (Kawamura and Yasui, 2005;Kundu et al., 2010b). The diurnal variation trend of C_2 was similar to that of C_3 and C_4, indicating that these compounds may have similar photochemical oxidation pathways or emission sources in the atmosphere.

C_9 diacid is the most abundant diacid in the range of C_7–C_{11} diacids, which is similar to that in marine aerosols from the southern and western Pacific Ocean (Wang et al., 2006). Such high abundance of C_9 diacid indicates that marine biogenic emissions and subsequent photochemical formation of organic aerosols were likely significant over the SCS and EIO, because C_9 diacid is a photochemical oxidation product of unsaturated fatty acids emitted from the productive marine regions (Bikkina et al., 2014;Hoque et al., 2017). In addition, the photochemical oxidation of C_9 diacid leads to the generation of its lower homologues including C_4–C_6 diacids (Kawamura et al., 1996b;Yang et al., 2008). Thus, the similar abundance of diacids (C_2 to C_6 and C_9) in the SCS and Malacca (Fig. 3) suggest that the 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 those 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. It was likely because the air masses arrived over EIO-SL and EIO-WI regions mostly originated from the remote oceanic regions and thus, the marine biogenic emission should be the major potential source of organic aerosols with no significant influence from the Asian outflow. Interestingly, the concentrations of C_9 diacid (average 68.9 ± 65.1 ng m^{-3}) in SLDP samples were several times higher than that observed in other regions over the SCS and EIO. As noted above, C_9 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_9 diacid in SLDP is likely derived by the oxidation of unsaturated fatty acids from mainland biota (Zhao et al., 2018). In fact, the terrestrial air masses that enriched with higher plant emissions and SOA produced upon subsequent oxidation of BVOCs during daytime should be transported onshore during nighttime by land breeze (Kang et al., 2017). In addition, the photochemical breakdown of C_9 diacid should be insignificant during nighttime.

Figure 3 shows the temporal variations in selected diacids over the SCS and EIO during the sampling periods. The temporal patterns of C_6 and C_9 diacids were similar (Fig. 3). C_6 diacid could be produced via the oxidation of cyclic olefins emitted from anthropogenic sources (e.g. fossil-fuel combustion) (Kawamura et al., 1996a), and could also be derived from photochemical breakdown of biogenic C_9 diacid (Kawamura et al., 1996c). Bikkina et al. (2015) concluded that the high mass concentrations of C_9 in marine aerosols were consistent with the high biological activity at the ocean surface. Such similar temporal variations in C_6 and C_9 diacids together with the results of backward trajectories (Fig. 1b) indicate that the formation of C_6 diacid is mostly from the photochemical breakdown of C_9 diacid which should have been derived from marine biogenic emissions. Based on ultraviolet (UV) irradiation of oleic acid and ozone system, Matsunaga et al. (1999) found a series of C_2 to 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 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 aging 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 should be mainly 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 those oceanic regions as reflected by low C_9 diacid loading.

Phthalic acid (Ph acid) is a tracer for anthropogenic organic aerosols. Concentrations of Ph acid over the SCS to EIO were much lower than that in urban Tokyo in summer (average 29 ng m^{-3}) (Kawamura and Yasui, 2005) and Chinese cities (90 ng m^{-3}) (Ho et al., 2007). Ph acid can be released directly from fossil fuel combustion (Kawamura and Kaplan, 1987). Secondary formation through 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 of EIO were not so seriously impacted by continental air masses from East and Southeast Asia. It was worth noting that Ph was more abundant in SLDP by several folds than other regions (Table 1), so we do not preclude the influence of anthropogenic emissions, particularly fossil fuel combustion, associated with the terrestrial air masses arrived in SLDP.

3.2.2 Oxocarboxylic acids

Oxocarboxylic acids (ωC_2−ωC_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). Being similar to diacids, oxocarboxylic acids are mainly derived from combustion sources, but can also be produced by photooxidation of various organic precursors in the atmosphere from anthropogenic and biological sources (Kawamura and Bikkina, 2016). The concentrations of total oxoacids ranged from 1.48 to 13.2 ng m^{-3} (average 6.51 ± 3.99 ng m^{-3}) in the SCS, 0.16-2.01 ng m^{-3} (0.96 ± 0.46 ng m^{-3}) in the EIO-WI, 0.23–5.06 ng m^{-3} (1.85 ± 1.51 ng m^{-3}) in the EIO-SL, 0.29–10.4 ng m^{-3} (4.22 ± 3.75 ng m^{-3}) in Malacca and 7.46–40.3 ng m^{-3} (24.0 ± 16.4 ng m^{-3}) in SLDP. The concentrations of total oxoacids are lower than those from Gosan, Jeju Island, South Korea (average 53 ng m^{-3}) (Kawamura et al., 2004) and urban sites in China (45 ng m^{-3}) (Ho et al., 2007). The concentrations of oxoacids were lower in the EIO-WI than the other regions (Table 1). The spatial distributions of ω-oxoacids showed a pattern of SLDP > SCS > Malacca > EIO-SL > EIO-WI, being consistent with those of major diacids (C_2, C_3, and C_4), which indicated that these oxoacids were potential precursors of dicarboxylic acids (Sempére and Kawamura, 1994).

Glyoxylic acid (ωC_2) was the most abundant oxoacid followed by pyruvic acid (Pyr) acid (Table 1). All of them are important intermediates in photo-oxidation processes and are used in the production of low carbon-number diacids such as C_2, C_3 and C_4 diacids (Hatakeyama et al., 1987). Several studies reported that Pyr is produced by in-cloud oxidation of isoprene in the atmosphere (Carlton et al., 2006;Carlton et al., 2009) that 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 α-dicarbonyls (glyoxal and methylglyoxal) varied over a wide range (0.56–20.2 ng m^{-3}) with relatively high abundance in the SCS (average 5.25±4.46 ng m^{-3}) and SLDP (average 7.35±3.58 ng m^{-3}). The average concentration of total α-dicarbonyls during the cruise was higher than those in super-micron and submicron aerosols collected over the North Pacific in summer (0.51±0.22 ng m^{-3} in more biologically influenced aerosols and 0.66±0.20 ng m^{-3} in less biologically influenced aerosols) (Miyazaki et al., 2010). The abundances of α-dicarbonyls were higher in the SCS and Malacca than those in the EIO-SL and EIO-WI, which were similar to diacids and oxoacids (Fig. 2 and 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 atmospheric oxidation of isoprene, emitted from the terrestrial vegetation and/or marine phytoplankton (Sorooshian et al., 2009). Besides, Gly is also a photochemical oxidation product of aromatic hydrocarbons from combustion of fossil fuels (Carlton et al., 2007;Volkamer et al., 2007). Both species can be existed in the aerosol phase and further oxidized to form less-volatile organic acids such as Pyr, ωC_2, and C_2 (Sorooshian et al., 2006). Therefore, the higher abundances of Gly and MeGly over the SCS than in other three regions could be due to enhanced continental outflow as well as the high biological activity in the sea surface. The spatial distributions of total oxoacids and α-dicarbonyls were similar to those of total diacids, indicating that they were similar in origin or formation mechanism (Kunwar et al., 2017). Based on the backward trajectory analysis, we identified four source regions of diacids and related compounds: (a) East Asia, (b) Southeast Asia, (c) the Bay of Bengal, and (d) the East 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 East Indian Ocean (i.e. EIO-WI), their concentrations was the lowest; and when the air masses originated from the Bay of Bengal and the East Indian Ocean (i.e. EIO-SL), the concentration of these compounds was between the former two.

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 over the SCS to EIO (SCS, EIO-WI, EIO-SL, Malacca and SLDP) are depicted in Fig 4. The percentage contributions of LMW-diacids (C_2–C_4) in total mass concentrations ($\Sigma(C_2–C_{12})$) varied from 96.4 to 98.9% (97.6±1.25%) in the SCS, 85.2 to 96.0% (90.6±5.38%) in the EIO-WI, 90.6 to 99.4% (95.0±4.44%) in the EIO-SL, 94.2 to 98.0% (96.1±1.88%) in Malacca, and 72.0 to 95.0% (83.5±11.5%) in SLDP. Interestingly, the relative abundances of C_2 to total mass concentrations of C_2 to 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 other four regions with the lower value in SLDP, whereas that of C_9 diacid was the opposite.

Figure 5 presents the relative abundances of the sums of short-chain diacids (C_2–C_4), long-chain diacids (C_5–C_{12}), unsaturated diacids (M, F, mM, Ph, iPh, and tPh), diacids containing additional functional group (hC_4, kC_3, and kC_7), oxoacids (ωC_2−ωC_9 and Pyr) and α-dicarbonyls (MeGly, 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% in the SCS and about 60% in the EIO-WI. Long-chain diacids were found to be second highest in SLDP and Malacca whereas that of α-dicarbonyls in the EIO-WI and EIO-SL, with high abundance in the SLDP and 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; while oxoacids were the highest in SLDP, followed by the EIO-WI, with the lowest values in the SCS and Malacca (Fig. 5). The high abundances of short-chain diacids indicate that the aerosols over the SCS to EIO were significantly aged during the long-distance transport, while the high abundances of long-chain diacids and α-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 in SLDP infer that the contributions from anthropogenic sources are also significant at SLDP.

3.4 Implications for origins and formation pathways

Different emission sources and the extent of aging lead to large differences in the concentrations of diacids and related compounds, and hence, mass concentration ratios of selected species can serve as effective markers for the identification of their origins and formation/transformation processes. Temporal variations in mass ratios of several organic acids as well as the relative abundance of C_2 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_3 diacid can be produced from C_4 diacid by oxidative reaction (Kawamura and Ikushima, 1993). There were robust relationships among C_2, C_3, and C_4 diacids in SCS, EIO-WI and EIO-SL regions, and between C_3 and C_4 diacids in Malacca (Table 3), suggesting that they should have been derived from similar sources. The C_3/C_4 ratio can be used as an effective marker to assess the extent of organic aerosol aging (Kawamura and Ikushima, 1993). The C_3/C_4 ratios were reported to be low (0.25–0.44) in vehicular emissions, because the C_3 diacid is thermally unstable to be easily degraded during combustion (Kawamura and Kaplan, 1987). In contrast, the C_3/C_4 ratios reported to be high (range, 1.0–11, average 3.9) in marine aerosols collected from the North Pacific (including tropics), which have been considered to be photochemically aged during the atmospheric transport (Kawamura and Sakaguchi, 1999). The C_3/C_4 ratios in this study ranged from 0.3 to 4.6 with an average value of 2.0. They are higher than those in urban aerosols from Chinese megacities (0.6–1.1, average 0.74) (Ho et al., 2007), Tokyo (0.56–2.9, average 1.6) (Kawamura and Ikushima, 1993) and New Delhi, India (0.40–1.1; average 0.66 in daytime and 0.58 in nighttime) (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—potentially owing to photochemical processing (Fu et al., 2013a). Therefore, such higher C_3/C_4 ratios suggest that the organic aerosols over the SCS to EIO are significantly subjected for intensive photochemical aging during the atmospheric long-range transport of 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 to C_3 diacid was enhanced at lower latitudes due to the increase of temperature and solar radiation. However, such a trend did 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. Such 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 aging (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 are higher than those reported in Chinese cities (average 7.1) (Ho et al., 2007), Sapporo (average 3.1) (Aggarwal and Kawamura, 2008), and South Korea (average 8.6) (Kundu et al., 2010b). Such a result indicates that C_2 could be largely generated by the photochemical degradation of C_4 diacid. Also, a significant correlation was found between relative abundance of C_2 (C_2 %) and C_2/C_4 mass ratio (Fig. S2c), suggesting the potential formation of C_2 diacid from photochemical breakdown of C_4 diacid. A concurrent trend (Fig. 6c) was also obtained for the increased contribution of C_2 to total aliphatic diacids ($C_2/\Sigma(C_2–C_{12})$), suggesting more photochemical aging of organic aerosols in low latitudes with stronger solar radiation.

The $C_2/\Sigma(C_2–C_{12})$ ratio has also been considered as an indicator to the degree of organic aerosols aging during long-distance 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 are (Kawamura and Sakaguchi, 1999). The $C_2/\Sigma(C_2–C_{12})$ was higher (0.76±0.06) in the SCS than that in the EIO-SL (0.74±0.08) and Malacca (0.71±0.11), followed by the EIO-WI (0.65±0.11) and SLDP (0.60±0.11). It is lower than that (0.8±0.04) reported in wintertime and higher than in summertime (0.5±0.01) Himalayan aerosols (Hegde and Kawamura, 2012). These results indicate that the organic aerosols in the SCS should have been more aged and/or influenced by anthropogenic emissions from East Asia, whereas in the EIO-WI and Malacca the aging of organic aerosols might be less intensive and influenced by only the marine biogenic emissions. Whilst in SLDP, the low $C_2/\Sigma(C_2–C_{12})$ should have been driven by the local coastal biota and the terrestrial biogenic and anthropogenic emissions as well as the less aging, particularly in the nighttime.

Maleic acid (M, *cis*-form) is transformed to fumaric acid (F, *trans*-form) with enhanced photochemical activity and hence, the mass ratio of M/F has been considered as a proxy to assess the degree of aerosol aging (Kawamura and Sakaguchi, 1999). In general, low M/F values reflect secondary oxidation as an important source. M/F ratios (0.07–0.73) were found to be lower in the EIO-WI than other (0.9–2.3) regions (Table 2). The mean value of M/F 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 in SLDP. They were all lower than those in Xi'an aerosols (summer: 2.22, winter: 2.38), and were about the same or less than those reported at the Korean Gosan site (spring: 1.38, summer: 0.76, autumn: 1.62, winter: 2.21), which have been considered to be aged, indicating that the aging 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, and thus the *cis*-*trans* transformation is 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 insights into the relative strengths of biogenic and anthropogenic sources in the given area. C_6/C_9 ratios (Fig. 6f) showed lower values in the EIO (except sample No. 2), which can be attributed to large influence of the marine air masses containing fatty acids like oleic acid, a precursor of C_9 diacid (Kawamura and Gagosian, 1987). Temporal variations in Ph/C_9 ratios over the SCS to EIO are shown in Fig. 6g, with the averages of 2.02 in the SCS, 1.56 in the EIO-WI, 1.22 in the EIO-SL, and 0.90 in Malacca. They were lower than that (5.71) reported in wintertime Gosan aerosols from South Korea (Kundu et al., 2010a), but higher than these in summertime (1.7) and wintertime (1.78) aerosols in Xi'an, China (Wang et al., 2012) and that 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_6 and C_9 diacids showed a positive correlation ($R = 0.51$, $p < 0.0001$) among all samples, indicating that C_6 should also be significantly derived from photo-oxidation of BVOCs such as cyclic olefins. The higher Ph/C_9 ratios found over the SCS than in other regions (Fig. 6g) again suggest that the contribution from fossil-fuel combustion is also significant, 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_2 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, those ratios were insignificant except $\omega C_2/C_2$ (Fig. 6). Such spatial distributions of 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 should have been influenced by the marine biogenic emissions and their subsequent oxidation processes. In addition, there were good correlations among Pyr, ωC_2 and MeGly in the SCS and Malacca, while the correlations were poor in the samples from EIO-WI and EIO-SL (except for Pyr and MeGly in EIO-WI, and ωC_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 the SCS and Malacca where were affected by anthropogenic emissions.

Finally, to better understand the enhanced emission of unsaturated fatty acids and BVOCs from the biologically active ocean surface over the SCS to EIO, we presented the satellite image of Chlorophyll-a loading in the EIO in

Fig. 1a. The concentrations of Chlorophyll-a in the SCS and Malacca were high. Interestingly, high concentrations of diacids and related compounds (Fig. 3) were consistent with high concentrations of Chlorophyll-a in the marine surface. This consistency indicates that high abundances of diacids in the SCS and Malacca attribute to firstly the oceanic emissions of BVOCs from high biological area and secondly the oxidation during atmospheric transport, rather than the influence of anthropogenic emissions associated with the continental outflow.

3.5 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 those in the EIO-WI and EIO-SL regions (Fig. 3j). As discussed above, such high abundance of WSOC in the SCS and Malacca may be caused by enhanced aging of organic compounds from the surface ocean by high biological activities and then subsequent oxidation to produce more water-soluble organics. In this study, the spatial/temporal trends of diacids and related compounds are generally consistent with that of OC, EC and WSOC, which are high in the SCS and low in other regions. The fractions of some major diacids, oxoacids and α-dicarbonyls in WSOC and OC are presented in Table 5. The total diacids account for 12.0 ± 5.75% (range 2.00–32.4%) of WSOC over the EIO. Whilst, the fractions of oxoacids and α-dicarbonyls in WSOC ranged from 0.03 to 1.22% (average 0.34 ± 0.20%) and 0.02–3.12% (0.60 ± 0.68%), respectively. In addition, a strong linear correlation was found between WSOC and C_2 diacid (Table 4), which suggests that the WSOC was mainly generated by secondary formation, rather than biomass-burning emissions associated with the Asian outflow.

4 Conclusions

The dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in marine aerosols collected over the SCS to EIO from 10 March to 26 April 2015 provided new insight on their origins and formation processes in tropical regions. The spatial distribution of diacids showed high concentrations in nearshore regions (the SCS, Malacca, SLDP) and relatively low in the remote regions (the EIO-WI and EIO-SL). Their molecular distributions were characterized by the dominance of C_2 diacid. The anthropogenic pollutants under the Asian outflow strongly influenced the concentrations of dicarboxylic acids in the SCS and Malacca whereas the oceanic biogenic emissions and subsequent oxidation influenced the distributions of those species in the EIO-WI and EIO-SL. A close relationship in the temporal variability of C_9, C_6 and total concentration of short-chain diacids (C_2−C_4) implied that the in-situ secondary formation of long-chain (including C_3 and C_4) diacids and related compounds was significant rather than the photochemical breakdown of higher diacids to their lower homologues over the SCS to EIO, despite significant aging of the air masses transported from the terrestrial region, due to enhanced emissions of VOCs from marine biota over the region. This finding was also supported by good linear relationships among C_4, hC_4, and C_3 diacids. The positive correlations obtained between C_2% and C_2/C_4 ratios and negative correlations between C_2% and C_3% as well as C_4% indicated that the formation of C_2 from C_4 diacid *via* C_3 is significant. Further, 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/Malacca and EIO-WI/EIO-SL, respectively. These results combined with 5-day backward air mass trajectories and the satellite image of Chlorophyll-a suggest 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 the sources mentioned above. In addition, terrestrial biogenic and anthropogenic emissions might had played significant role on the loading of diacids and related compounds at SLDP. Further work on the chemical characterization of the marine organic aerosols at a molecular level by high-solution MS such as Orbitrap and FT-ICR MS are needed to obtain the detailed information on sulfur-containing organics from both biogenic and anthropogenic sources.

Data availability. The dataset for this paper is present in the Tables and Figures and is available upon request from the corresponding author (fupingqing@tju.edu.cn).

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

Author contributions. PF designed this research. Samples were collected by LW. Laboratory analyses were performed by JY and WZ. The manuscript was written by JY, PF and CMP with consultation from all other authors.

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Table 1. Summary of concentrations (ng m^{-3}) of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls as well as concentrations (μg m^{-3}) of EC and OC in TSP samples collected during the NORC2015-10 cruise over the South China Sea to the East Indian Ocean.

Species	SCS (n = 27)		EIO-WI (n = 20)		EIO-SL (n = 28)		Malacca (n = 9)		SLDP (n = 3)	
	Range	Avg±SD	Range	Avg±SD	Range	Avg±SD	Range	Avg±SD	Range	Avg±SD
Dicarboxylic acids										
Oxalic, C_2	30.3–626	233±143	4.43–70.1	18.2±18.4	5.21–232	58.2±55.3	14.5–373	145±112	179–454	303±140
Malonic, C_3	2.14–87.9	36±23	0.34–11.4	2.09±2.52	0.76–42.1	8.19±9.95	2.57–74.0	24.2±25.4	25.9–55.4	42.2±15.0
Succinic, C_4	1.73–50.4	18±14	0.23–6.4	1.35±1.65	0.57–20.6	4.33±4.86	1.18–72.9	18.0±22.7	14.1–78.5	45.2±32.2
Glutaric, C_5	0.23–8.52	2.60±2.15	bdl–0.79	0.23±0.19	bdl–1.69	0.48±0.46	bdl–9.53	3.49±3.70	2.94–14.6	8.82±5.85
Adipic, C_6	0.13–4.09	1.11±0.93	0.17–0.83	0.42±0.22	0.03–1.18	0.31±0.29	0.01–3.59	1.28±1.36	1.95–7.17	4.76±2.63
Pimelic, C_7	bdl–1.88	0.58±0.60	bdl–0.22	0.03±0.07	bdl–0.50	0.12±0.17	bdl–1.30	0.43±0.46	bdl–0.45	0.28±0.25
Suberic, C_8	bdl	bdl	bdl–0.09	0.004±0.0	bdl–14.3	0.51±2.71	bdl	bdl	bdl	bdl
Azelaic, C_9	bdl–6.97	1.82±1.57	bdl–2.22	0.45±0.49	0.09–15.1	1.25±2.75	0.32–3.96	1.82±1.29	11.7–140	68.9±65.1
Sebacic, C_{10}	bdl–2.69	0.28±0.53	bdl–0.82	0.29±0.24	bdl–9.06	0.57±1.68	bdl–1.10	0.58±0.46	0.66–3.43	2.00±1.39
Undecanedioic, C_{11}	bdl–0.16	0.02±0.05	bdl–0.69	0.16±0.15	bdl–0.38	0.13±0.10	bdl–0.38	0.20±0.15	bdl–1.64	0.62±0.89
Dodecanedioic, C_{12}	bdl	bdl	bdl–0.35	0.02±0.08	bdl	bdl	bdl–0.29	0.06±0.11	bdl	bdl
Methylmalonic, iC_4	bdl–2.26	0.95±0.65	bdl–0.29	0.01±0.06	bdl–0.82	0.14±0.23	bdl–3.29	0.93±1.06	1.02–2.47	1.94±0.79
Methylsuccinic, iC_5	0.30–3.37	1.46±0.98	0.08–0.54	0.35±0.12	0.13–1.18	0.56±0.30	0.21–3.56	1.63±1.28	2.61–10.1	6.99±3.89
Methylglutaric, iC_6	bdl–0.68	0.05±0.18	bdl–0.18	0.02±0.05	bdl	bdl	bdl–0.59	0.26±0.25	0.67–3.29	1.84±1.33
Maleic, M	0.12–2.70	0.93±0.67	0.07–0.55	0.19±0.11	0.08–1.02	0.28±0.22	0.04–1.42	0.77±0.59	1.58–4.14	2.56±1.38
Fumaric, F	0.17–2.16	0.74±0.48	0.16–1.45	0.77±0.32	0.05–0.82	0.28±0.22	0.08–1.07	0.39±0.33	0.81–2.49	1.49±0.89
Methylmaleic, mM	0.17–2.13	0.82±0.48	0.17–0.76	0.39±0.15	0.06–0.96	0.32±0.21	0.11–1.33	0.73±0.47	2.26–5.49	3.80±1.62
Phthalic, Ph	0.16–6.57	2.29±1.89	bdl–1.25	0.50±0.34	0.06–2.95	0.77±0.59	0.26–3.56	1.64±1.23	8.63–13.2	10.8±2.31
Isophthalic, iPh	bdl–0.60	0.05±0.16	bdl–0.37	0.02±0.08	bdl–0.22	0.02±0.06	bdl–0.49	0.12±0.20	1.08–2.73	1.99±0.84
Terephthalic, tPh	bdl–2.12	0.22±0.57	bdl–1.25	0.13±0.17	bdl–0.38	0.03±0.09	bdl–0.59	0.10±0.21	bdl–1.76	0.59±1.02
Malic, hC_4	bdl–2.25	0.62±0.53	bdl–0.72	0.05±0.17	bdl–0.81	0.13±0.23	bdl–1.05	0.31±0.35	0.88–1.95	1.45±0.54
Ketomalonic, kC_3	bdl–5.84	1.76±1.34	bdl–0.83	0.22±0.22	0.05–2.10	0.54±0.47	0.15–2.19	1.00±0.90	1.15–2.75	2.06±0.82
4-Ketopimelic, kC7	bdl–7.75	1.85±1.70	bdl–0.63	0.12±0.19	bdl–1.87	0.45±0.56	0.17–9.27	3.59±3.68	1.24–3.34	2.50±1.10
Subtotal	44.6–759	305±186	8.28–96.3	26.1±23.3	8.55–294	77.6±73.1	21.9–501	207±158	259–708	514±231
Oxocarboxylic acids										
Pyruvic, Pyr	0.01–1.70	0.60±0.42	bdl–0.70	0.30±0.17	0.11–0.75	0.33±0.19	bdl–1.23	0.46±0.44	0.83–1.62	1.13±0.42
Glyoxylic, ωC_2	0.41–9.23	2.68±1.87	bdl–0.75	0.23±0.23	0.09–2.89	0.97±0.86	0.003–4.92	2.05±2.08	3.56–8.65	6.28±2.56
3-Oxopropanoic, ωC3	0.14–2.53	0.86±0.56	0.06–0.65	0.27±0.14	bdl–0.75	0.25±0.26	bdl–2.01	0.56±0.61	0.55–2.16	1.13±0.90
4-Oxobutanoic, ωC4	bdl–1.09	0.29±0.41	bdl	bdl	bdl–1.42	0.06±0.27	bdl–2.66	0.72±1.02	1.41–9.27	5.10±3.95
5-Oxopentanoic, ωC5	bdl–0.09	0.01±0.03	0.05–0.39	0.13±0.08	bdl–0.15	0.04±0.03	bdl–0.15	0.04±0.05	0.07–0.21	0.16±0.07
7-Oxoheptanoic, ωC7	bdl–0.23	0.23±0	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
8-Oxooctanoic, ωC8	bdl–3.94	1.37±1.44	bdl	bdl	bdl	bdl	bdl–0.23	0.07±0.10	bdl–16.1	8.47±8.07
9-Oxononanoic, ωC9	bdl–1.89	0.69±0.65	bdl–0.29	0.03±0.07	bdl–1.41	0.19±0.36	bdl–0.88	0.32±0.32	0.80–2.38	1.72±0.83
Subtotal	1.48–13.2	6.51±3.99	0.16–2.01	0.96±0.46	0.23–5.06	1.85±1.51	0.29–10.4	4.22±3.75	7.46–40.3	24.0±16.4
α-Dicarbonyls										
Glyoxal, Gly	0.05–7.70	2.28±2.26	0.20–3.20	1.64±0.67	0.11–2.02	0.87±0.40	0.26–0.87	0.52±0.23	2.70–7.04	4.15±2.50
Methylglyoxal, MeGly	0.29–20.0	2.97±3.72	0.88–3.01	1.66±0.54	0.09–7.45	1.22±1.31	0.93–4.01	1.81±0.93	2.31–4.45	3.20±1.11
Subtotal	0.56–20.2	5.25±4.46	1.08–5.29	3.31±1.01	0.95–8.86	2.08±1.47	1.18–4.79	2.34±1.06	5.04–11.5	7.35±3.58
Carbonaceous components										
OC	0.18–2.63	1.26±0.67	0.02–0.66	0.27±0.19	0.06–1.69	0.59±0.45	0.28–4.44	2.02±1.54	3.57–20.9	12.8±8.73
EC	0.05–0.75	0.27±0.15	0.01–0.13	0.05±0.05	0.04–0.91	0.21±0.18	0.07–0.63	0.24±0.18	1.67–7.57	4.24±3.02
WSOC	0.22–2.31	1.05±0.65	0.05–0.58	0.15±0.12	0.06–1.00	0.35±0.25	0.09–2.72	1.15±0.92	1.12–7.44	4.43±3.17

bdl: below detection limit, which is ca. 0.005 ng m^{-3} for the target compounds.

Table 2. Diagnostic mass ratios of selected diacids and related compounds in TSP samples collected during the NORC2015-10 cruise.

Mass Ratio	SCS	EIO-WI	EIO-SL	Malacca	SLDP
			Avg ± SD		
C_2/C_4	16.2±8.14	17.1±10.6	16.1±6.72	15.1±12.4	8.28±3.80
C_3/C_4	2.18±0.95	1.79±0.90	2.05±0.80	1.99±1.14	1.23±0.63
$C_2/\omega C_2$	101±69.8	146±220	69.7±41.2	721±1678	48.1±5.79
C_2/Pyr	580±499	70.3±63.7	193±191	294±254	267±71.0
$C_2/\Sigma(C_2–C_{12})$	0.80±0.05	0.76±0.07	0.78±0.07	0.76±0.11	0.65±0.12
$C_3/\Sigma(C_2–C_{12})$	0.12±0.04	0.09±0.02	0.11±0.03	0.12±0.05	0.09±0.02
$C_4/\Sigma(C_2–C_{12})$	0.06±0.02	0.06±0.03	0.06±0.04	0.08±0.06	0.09±0.03
C_6/C_9	0.76±0.93	1.17±0.76	0.49±0.52	0.49±0.39	0.11±0.07
Ph/C_9	2.02±4.26	1.66±1.33	1.22±1.19	0.90±0.21	0.34±0.34
M/F	1.33±0.52	0.29±0.19	1.30±0.59	2.08±1.72	1.77±0.17
C_2/MeGly	129±156	11.3±10.6	57.9±40.8	81.9±55.5	92.1±13.1
C_2/Gly	681±1466	14.6±15.2	127±196	295±184	77.4±21.2
Gly/MeGly	0.86±0.67	1.02±0.45	1.43±2.31	0.31±0.12	1.24±0.32

Table 3. Correlation matrices of selected diacids and related compounds in TSP collected during the NORC2015-10 cruise.

Correlation	C_2	C_3	C_4	C_5	C_6	C_9	Ph	Pyr	ωC_2	MeGly
SCS (n=27)										
C_2	1.00									
C_3	0.85 **	1.00								
C_4	0.79 **	0.88 **	1.00							
C_5	0.86 **	0.73 **	0.87 **	1.00						
C_6	0.87 **	0.67 **	0.75 **	0.95 **	1.00					
C_9	0.67 **	0.38	0.36	0.70 **	0.78 **	1.00				
Ph	0.70 **	0.54 **	0.72 **	0.86 **	0.84 **	0.59 **	1.00			
Pyr	0.50 **	0.44 *	0.55 **	0.52 **	0.43 *	0.19	0.52 **	1.00		
ωC_2	0.88 **	0.71 **	0.68 **	0.80 **	0.79 **	0.68 **	0.69 **	0.66 **	1.00	
MeGly	0.65 **	0.40 *	0.30	0.42*	0.49 *	0.50 **	0.50 **	0.59 **	0.80 **	1.00
EIO-WI (n=20)										
C_2	1.00									
C_3	0.90 **	1.00								
C_4	0.89 **	0.94 **	1.00							
C_5	0.85 **	0.83 **	0.76 **	1.00						
C_6	0.26	0.37	0.41	0.41	1.00					
C_9	0.34	0.36	0.36	0.39	0.51 *	1.00				
Ph	0.11	0.29	0.18	0.51 *	0.67 **	0.40	1.00			
Pyr	0.10	0.13	0.14	0.17	0.04	0.33	0.04	1.00		
ωC_2	0.68 **	0.51 *	0.53 *	0.71 **	–0.04	0.40	0.12	0.23	1.00	
MeGly	0.11	0.13	0.13	0.00	0.21	0.28	–0.11	0.61 **	–0.12	1.00
EIO-SL (n=28)										
C2	1.00									
C_3	0.89 **	1.00								
C_4	0.86 **	0.94 **	1.00							
C_5	0.73 **	0.75 **	0.78 **	1.00						
C_6	0.41 *	0.31	0.49 **	0.44	1.00					
C_9	0.31	0.14	0.20	0.31	0.39 *	1.00				
Ph	0.53 **	0.35	0.43 *	0.52 **	0.70 **	0.79 **	1.00			
Pyr	0.40 *	0.20	0.38 *	0.24	0.38 *	0.22	0.27	1.00		
ωC_2	0.79 **	0.55 **	0.65 **	0.61 **	0.50 **	0.51 **	0.69 **	0.64 **	1.00	
MeGly	0.21	0.21	0.09	0.11	0.14	0.07	0.19	0.32	0.14	1.00
Malacca (n=9)										
C_2	1.00									
C_3	0.65	1.00								
C_4	0.45	0.88 **	1.00							
C_5	0.69 *	0.76 *	0.87 **	1.00						
C_6	0.89 **	0.64	0.56	0.85 **	1.00					
C_9	0.87 **	0.71 *	0.60	0.81 **	0.96 **	1.00				
Ph	0.84 **	0.87 **	0.80 *	0.89 **	0.90 **	0.94 **	1.00			
Pyr	0.55	0.71 *	0.83 **	0.79 *	0.60	0.56	0.71 *	1.00		
ωC_2	0.80 **	0.75 *	0.80 **	0.97 **	0.91 **	0.86 **	0.91 **	0.84 **	1.00	
MeGly	0.36	0.79 *	0.94 **	0.83 **	0.50	0.52	0.74 *	0.67	0.71 *	1.00

**: At 0.01 level (two-tailed), the correlation is significant.

*: At 0.05 level (two-tailed), the correlation is significant.

Table 4. 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_2	0.61–14.3 (4.78±2.63)	0.28–12.2 (3.52±2.34)
Malonic, C_3	0.14–2.82 (0.85±0.54)	0.07–2.41 (0.63±0.50)
Succinic, C_4	0.10–1.94 (0.54±0.37)	0.04–1.86 (0.41±0.34)
ΣC_2–C_4	1.02–22.0 (7.50±4.01)	0.47–18.8 (5.55±3.68)
ΣDiacids	2.00–32.4 (12.0±5.75)	0.92–27.7 (8.84±5.61)
ΣOxocarboxylic acids	0.03–1.22 (0.34±0.20)	0.01–1.93 (0.26±0.26)
Σα-Dicarbonyls	0.02–3.12 (0.60±0.68)	0.02–8.95 (0.47±1.08)

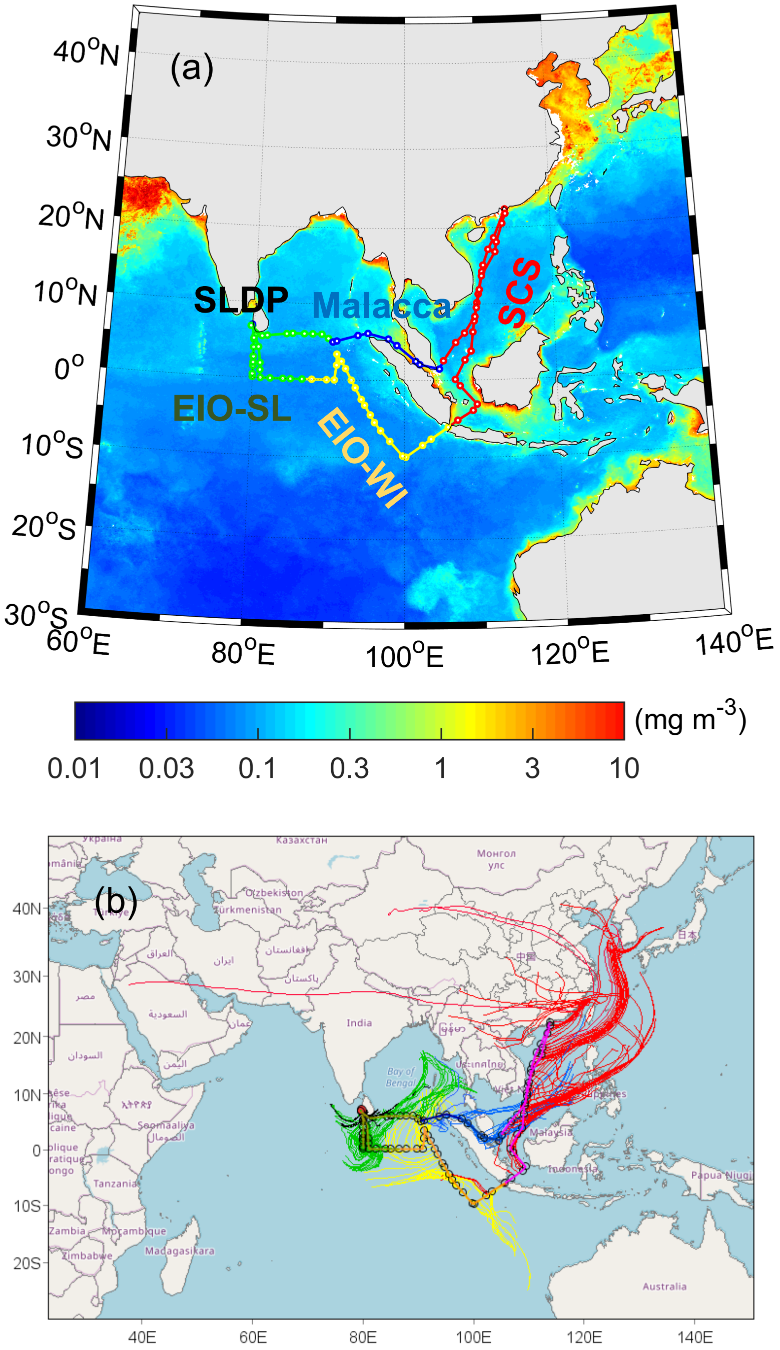


Figure 1. (a) Cruise tracks used for aerosols collection in the South China Sea and the East Indian Ocean during 10th March to 26th April 2015. The area where the red line is located is South China Sea (SCS), the yellow line is the East Indian Ocean near western Indonesia (EIO-WI), the green line is the East Indian Ocean near Sri Lanka (EIO-SL), the blue line is Malacca, and the red solid origins are the collection positions of three samples of Sri Lanka docking point (SLDP). The base map (©MATLAB) reflects an average composite of Chl*a* concentrations in March–April 2015 obtained from the NASA website at https://modis.gsfc.nasa.gov/data/dataprod/chlor a.php. (b) Air mass backward trajectories for the sampling days at arrival heights 100 m; the map was produced by the software © Meteoinfo.

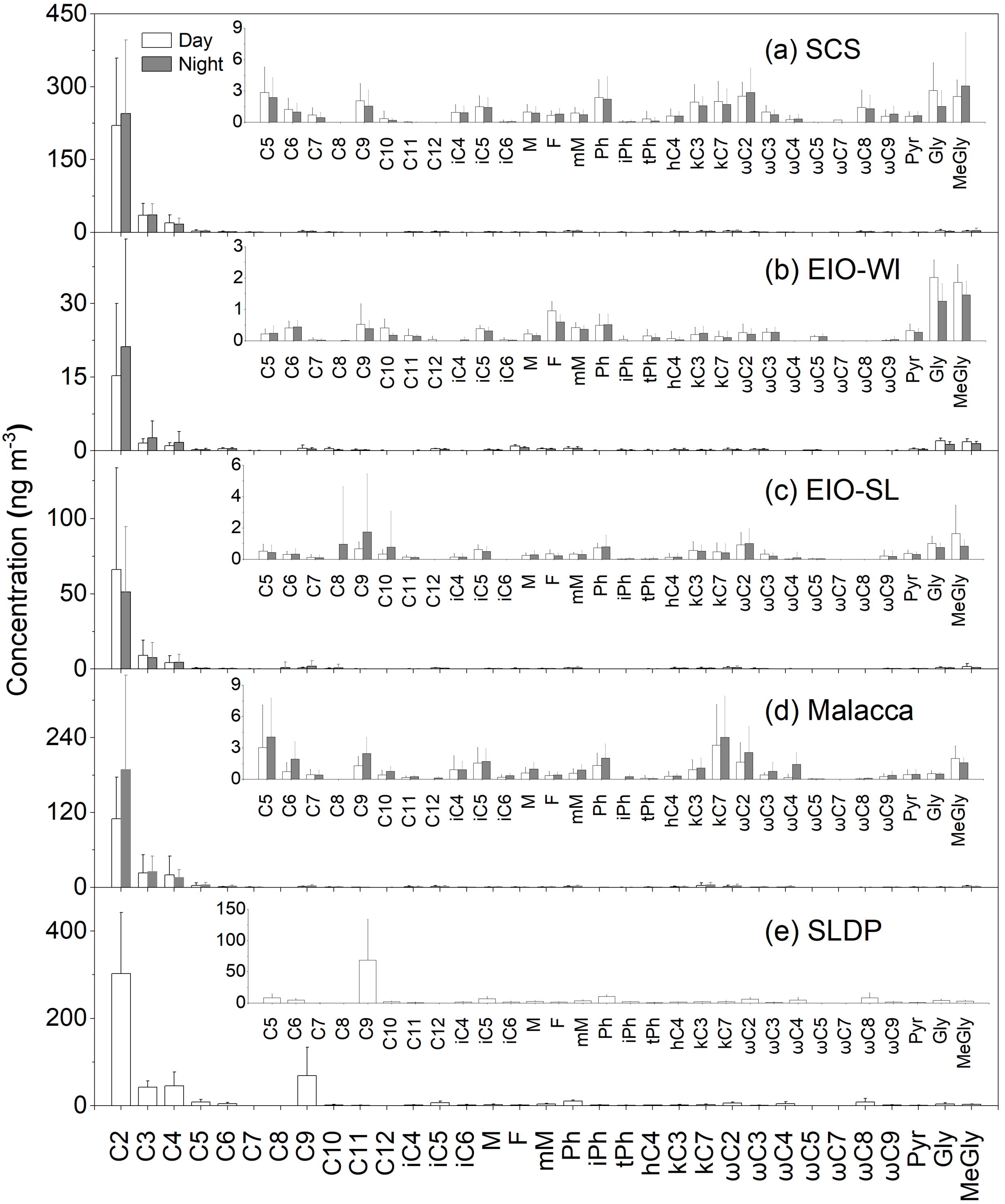


Figure 2. Molecular distributions of dicarboxylic acids and related compounds in TSP samples from (a) SCS, (b) EIO-WI, (c) EIO-SL, (d) Malacca, and (e) SLDP during 10th March to 26th April 2015.

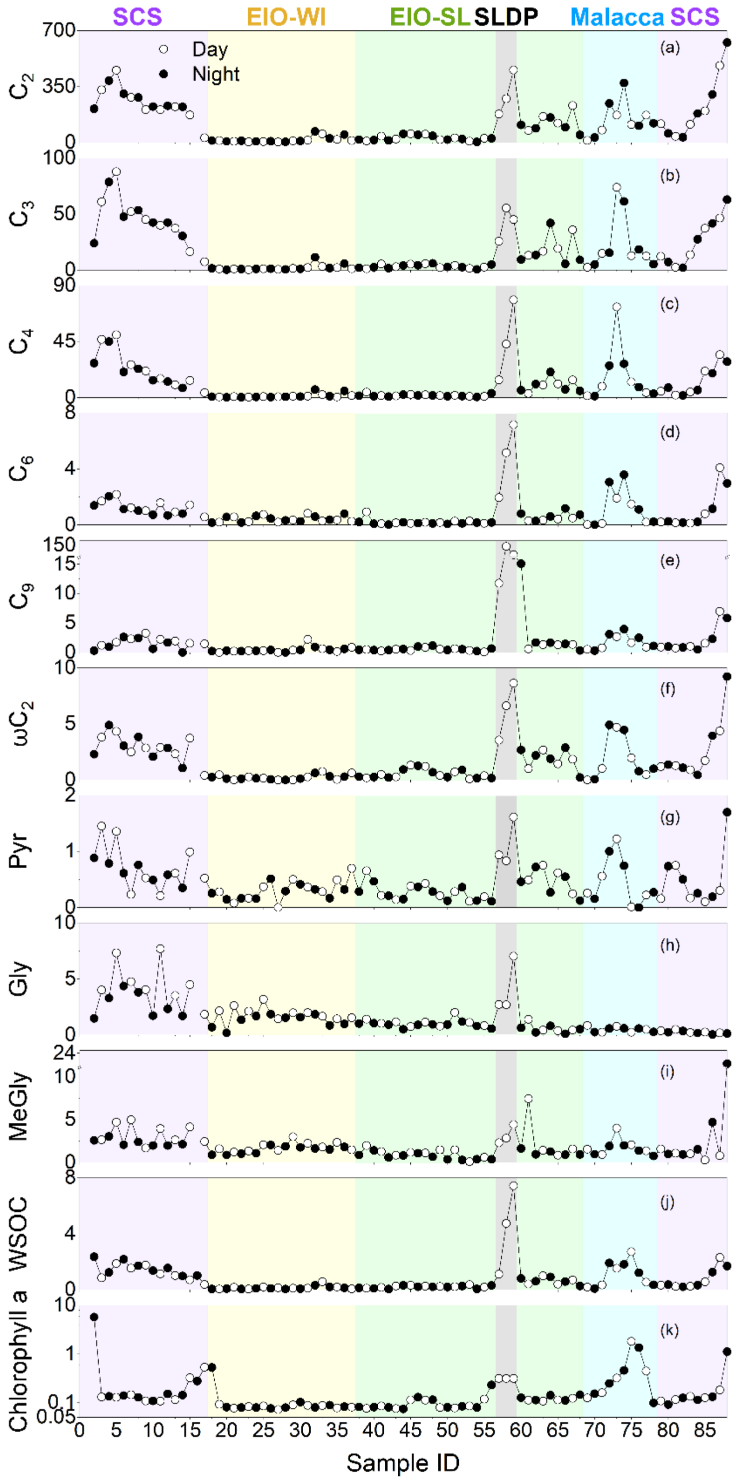
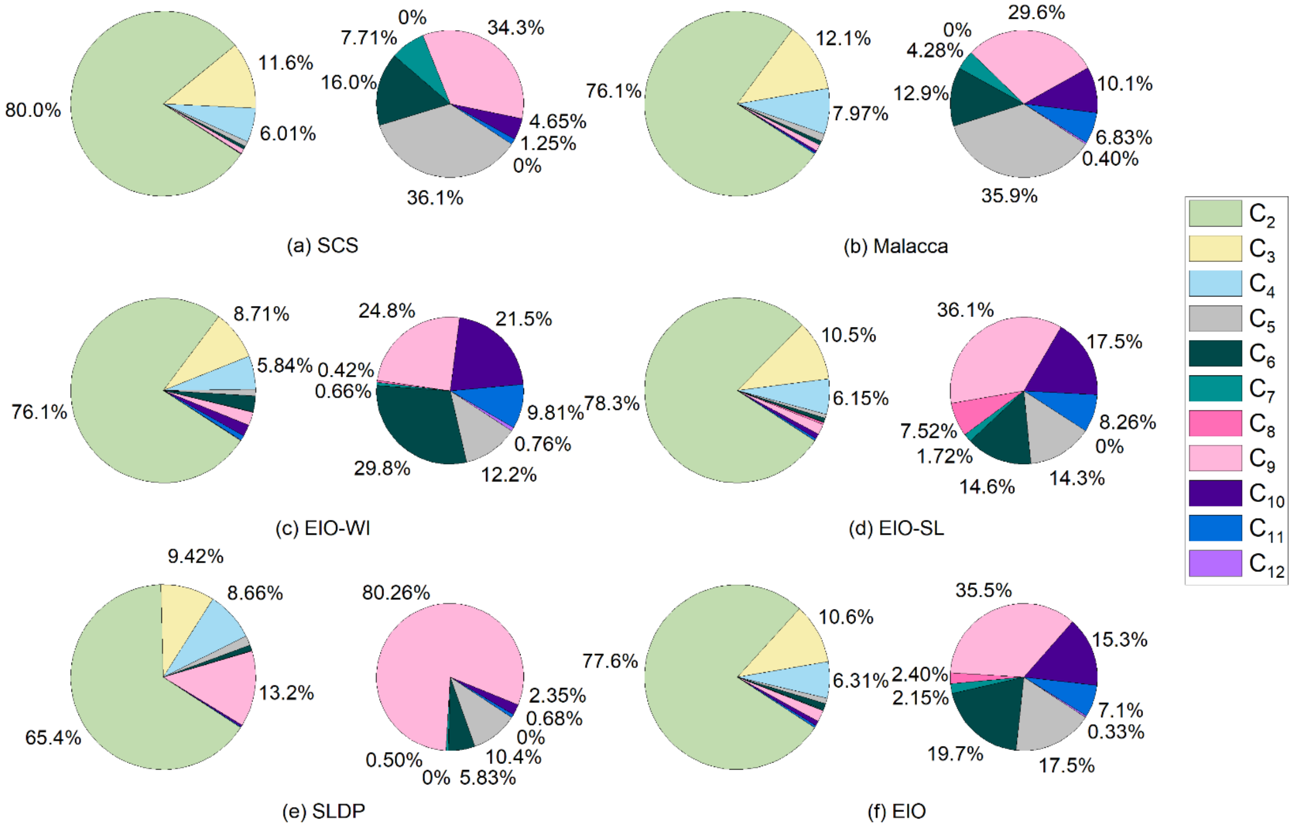


Figure 3. Daily variations in the concentrations of selected organic acids and water-soluble organic carbon (WSOC) in the TSP aerosols in South China Sea and the East Indian Ocean from 10th March to 26th April 2015 (all parameters are in ng m^{-3} except WSOC is in µg m^{-3} and Chlorophyll a is in mg m^{-3}).



(a) SCS

(b) Malacca

(c) EIO-WI

(d) EIO-SL

(e) SLDP

(f) EIO

Figure 4. Pie charts showing the percentage contribution of individual diacid to total aliphatic homologous diacids (ΣC_2–C_{12}) in different sea areas aerosols collected during the NORC2015-10 cruise.

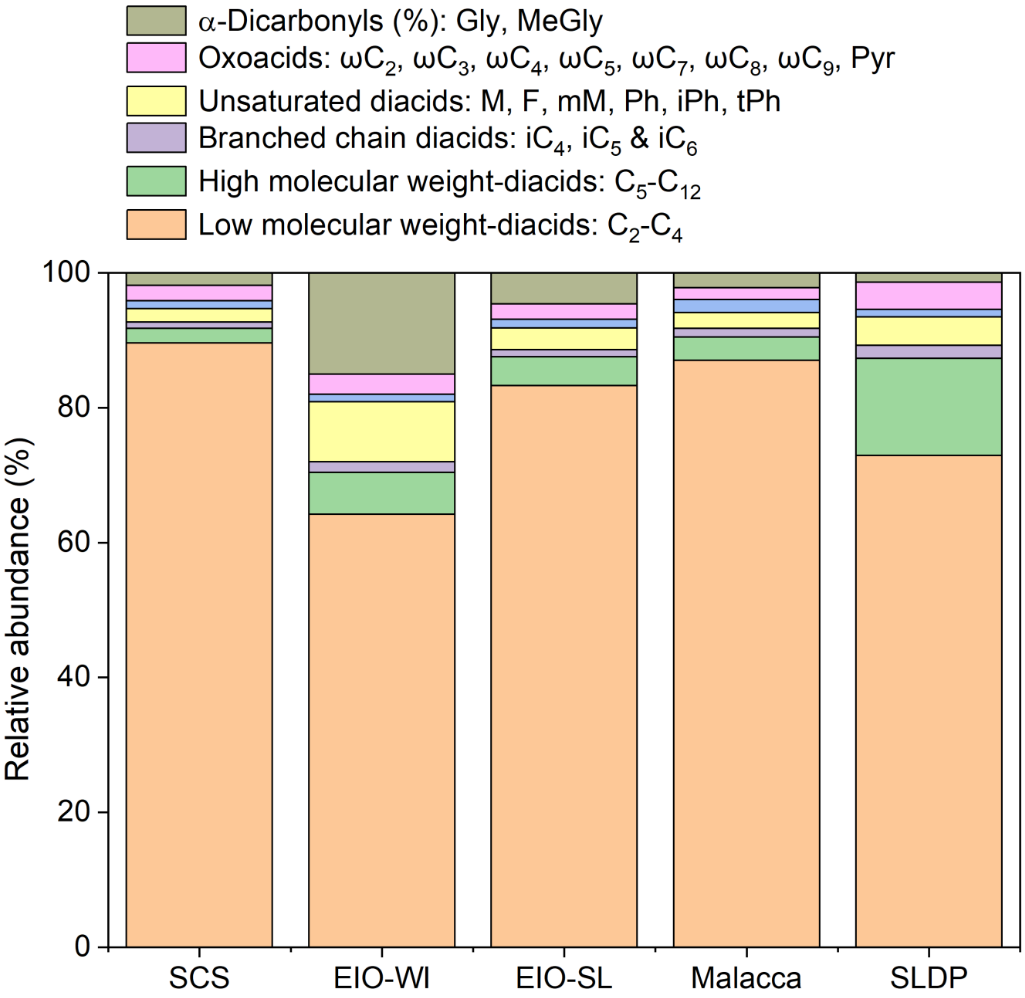


Figure 5. Relative abundances of individual compound class in the total diacids, oxoacids, and α-dicarbonyls in different sampling area aerosols collected during the NORC2015-10 cruise.

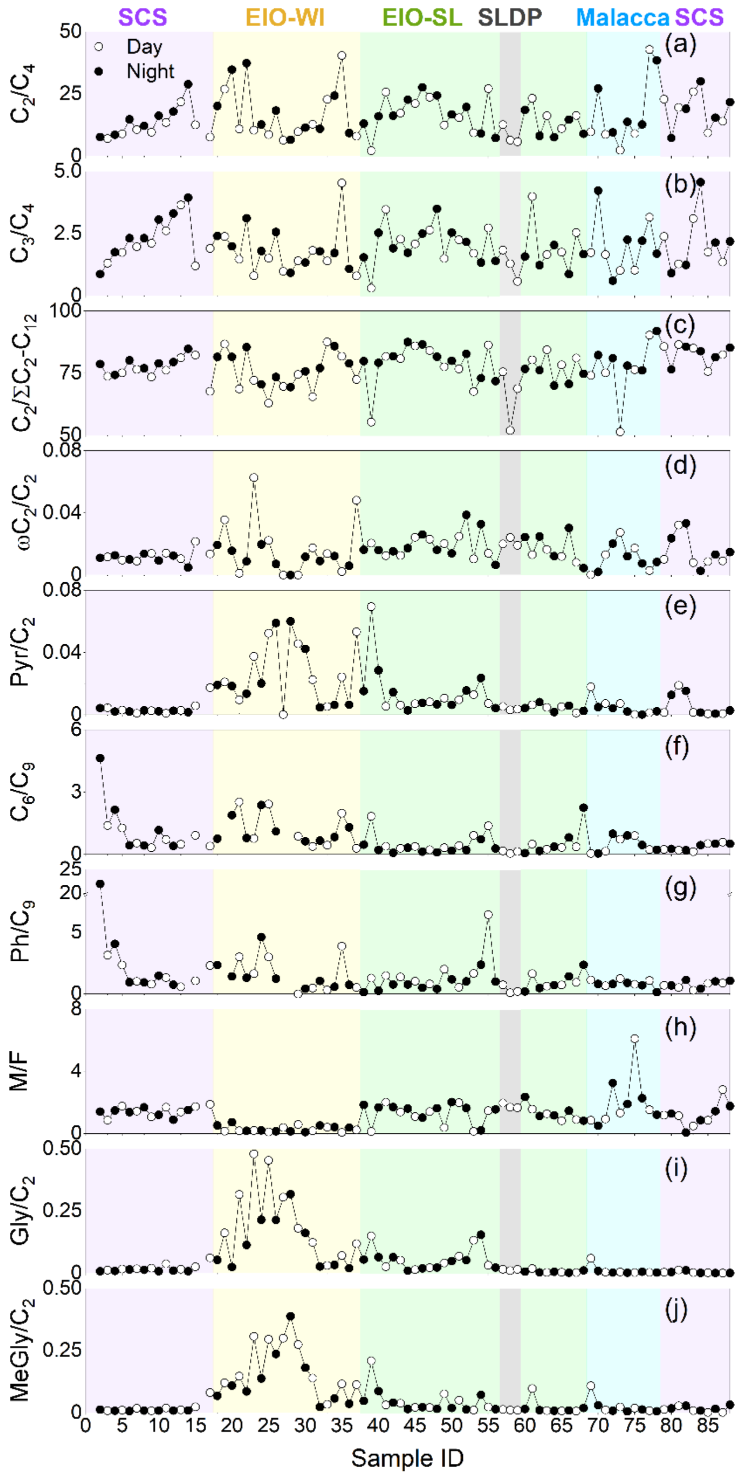


Figure 6. Daily variations in the concentration ratios of (a) C_2/C_4, (b) C_3/C_4, (c) $C_2/\Sigma C_2$–C_{12}, (d) $C_2/\omega C_2$, (e) C_6/C_9, (f) C_6/C_9, (g) Ph/C_9, (h) M/F, (i) C_2/Gly, and (j) $C_2/MeGly$ in TSP samples collected during the NORC2015-10 cruise.

Supporting Information to

Molecular and spatial distributions of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls in marine aerosols over the South China Sea to East Indian Ocean

Jing Yang[1,2], Wanyu Zhao[2,4], Lianfang Wei[2], Qiang Zhang[1], Yue Zhao[1], Wei Hu[1], Libin Wu[1], Xiaodong Li[1], Chandra Mouli Pavuluri[1], Xiaole Pan[2], Yele Sun[2], Zifa Wang[2], Cong-Qiang Liu[1], Kimitaka Kawamura[3], and Pingqing Fu[1]

[1]Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, China
[2]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China
[3]Chubu Institute for Advanced Studies, Chubu University, Kasugai 487-8501, Japan
[4]College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing, 100049, China

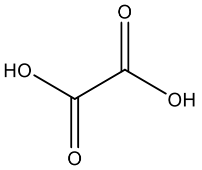
Correspondence to: Pingqing Fu (fupingqing@tju.edu.cn)

Linear correlations

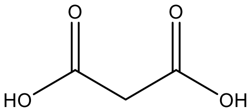
In order to further confirm the origins and formation pathways of diacids and related compounds, we examined the correlations between selected species and also conducted linear regression analyses for mass ratios of the selected chemical specie. Moderate correlations were observed for C_6 with C_9 diacids in the EIO-WI and EIO-SL, and significant correlations over the SCS and Malacca regions. Such positive correlations indicate that the C_6 diacid should have also been significantly generated from the biogenic VOCs such as cyclic olefins, in addition to the anthropogenic sources.

Hydroxy succinic acid (malic acid, hC_4), C_4 and C_3 diacids in the SCS correlated well each other ($p < 0.05$; $R^2 = 0.87$ for hC_4 *vs* C_3 and $R^2 = 0.78$ for hC_4 *vs* C_4; Fig. S2a and S2b). The formation of C_3 diacid from C_4 diacid through hC_4 as an intermediate has been proposed by (Kawamura and Sakaguchi, 1999) and also observed in a laboratory study (Yang et al., 2008). A very good linear relationship of hC_4 diacid with C_4 diacid ($R^2 = 0.85$) and C_2 diacid ($R^2 = 0.78$) has been reported in forest aerosols from central Europe, which have been attributed to *in-situ* photochemical production from biogenic unsaturated fatty acids (Kourtchev et al., 2009). Therefore, the good correlations observed among C_3, C_4 and hC_4 in the SCS implies that they were derived from common but mixed (both biogenic and anthropogenic) sources and the *in-situ* secondary formation might be more intensive, rather than the transformations from C_4 to C_3 via hC_4 diacids. A significant linear correlation was also found between methylmalonic (iC_4) acid with C_3 and C_4 diacids. The branched chain diacids could come from the oxidation of isoprene released from the ocean surface. Such linear correlations also suggest that the diacids and related compounds were photochemical oxidation products of isoprene and biogenic unsaturated fatty acids in the MABL, and also confirm the intensive *in-situ* secondary formation of diacids and related species. A notable feature observed here is the significant ($p < 0.05$) correlations between MeGly, Pyr, and ωC_2 with C_3 and C_4 diacids over Malacca, but not in other regions. Nguyen et al. (2010) found that C_3 and C_4 diacids were formed from isoprene oxidized by ozone based on the laboratory experiment. Furthermore, it has been reported that isoprene emission results in significant enhancement of SOA and O_3 levels at coastal U.S. sites (Gantt et al., 2010). Hence, the loading of C_3 and C_4 diacids also should have been influenced by not only the unsaturated fatty acids but also the isoprene, at least in Malacca region.

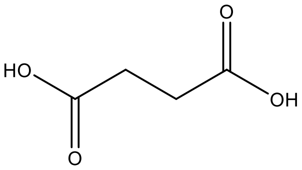
The $C_2/(\Sigma C_2–C_{10})$ ratios showed negative relationships with C_3 and C_4 diacids over the SCS to EIO (Fig. S3a and S3b). This phenomenon again confirms the formation of C_2 diacid from C_3 and C_4 diacids by their photochemical transformations during long-range atmospheric transport. It is also worth noting that the $C_4/(\Sigma C_2–C_{10})$ ratios showed a linear relationship with glutaric (C_5) acid in all regions, except the EIO-WI (Fig. S3c). Additionally, a similar variation trend is observed for the concentrations of C_5 and C_9 diacids in all regions, although they were not significant (C_9; Fig. S3d). Such positive relations reveal that they all should have been simultaneously produced significantly by in-situ photochemical reactions over the oceanic region, although we do not preclude the photochemical transformations of long-chain diacids to their lower homologues including C_6-C_4 diacids. Thus, the observed linear correlations among the relative abundances of C_2, C_3, C_4, C_5, and C_9 infer that the long-chain as well as C_3 and C_4 diacids were mainly derived from biogenic emissions followed by the in-situ secondary reactions whereas the C_2 diacid is mainly produced by the photochemical transformation of their higher over the SCS to EIO. The long-range transported air masses from the continental region that should be enriched with the anthropogenic emissions including oxidant species should have been promoted the oxidation of unsaturated fatty acids and BVOCs, resulting the enhanced levels of diacids and related compounds over the remote oceanic region.



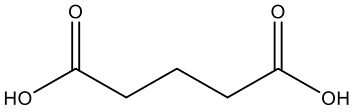
(a) Oxalic acid (C_2)



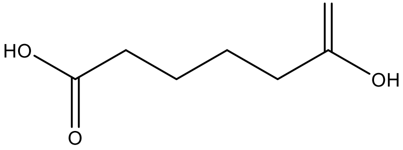
(b) Malonic acid (C_3)



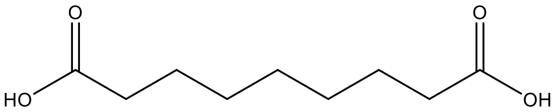
(c) Succinic acid (C_4)



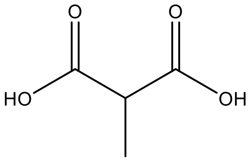
(d) Glutaric acid (C_5)



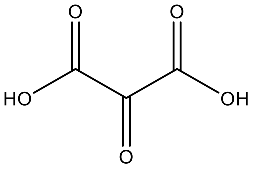
(e) Adipic acid (C_6)



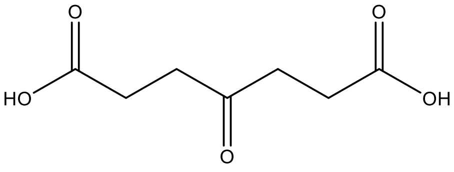
(f) Azelaic acid (C_9)



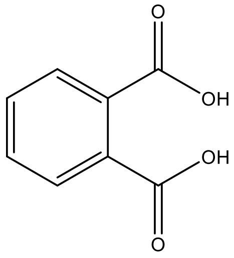
(g) Methylmalonic acid (iC_4)



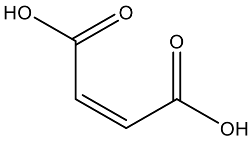
(h) Ketomalonic acid (kC_3)



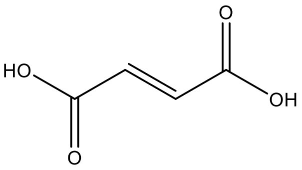
(i) 4-Ketopimelic acid (kC_7)



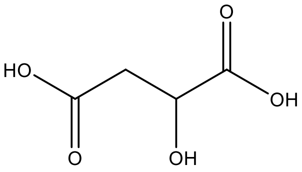
(j) Phthalic acid (Ph)



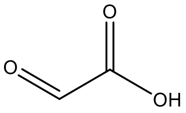
(k) Maleic acid (M)



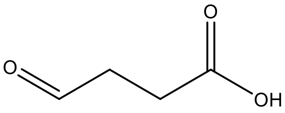
(l) Fumaric acid (F)



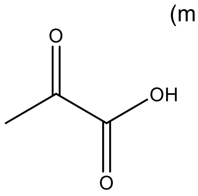
(m) Malic acid (hC_4)



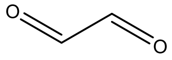
(n) Glyoxylic acid



(o) 4-Oxobutanoic acid



(p) Pyruvic acid (Pyr)



(q) Glyoxal (Gly)

Figure S1. Chemical structures of selected dicarboxylic acids and other major organic compounds detected in the marine aerosols.

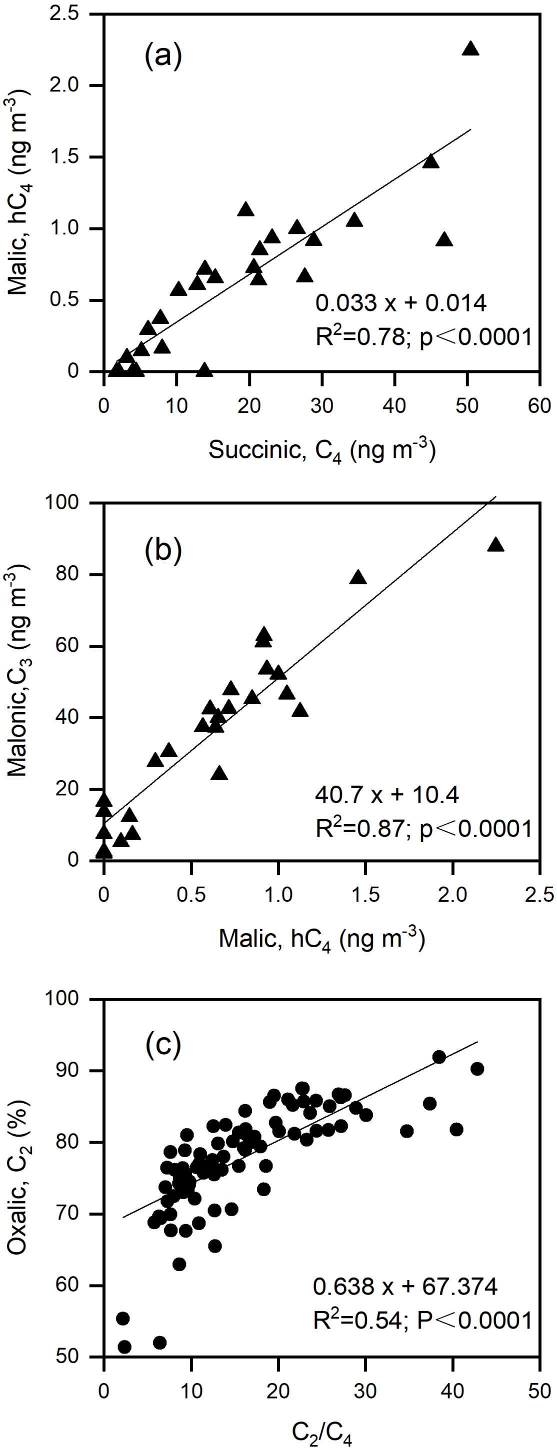


Figure S2. Scatterplots for (a) malic versus succinic acids, (b) malonic versus malic acids in aerosols collected over the SCS; (c) relative abundance of oxalic acid in total diacid mass versus C_2/C_4 ratios in aerosols collected over the all sea areas.

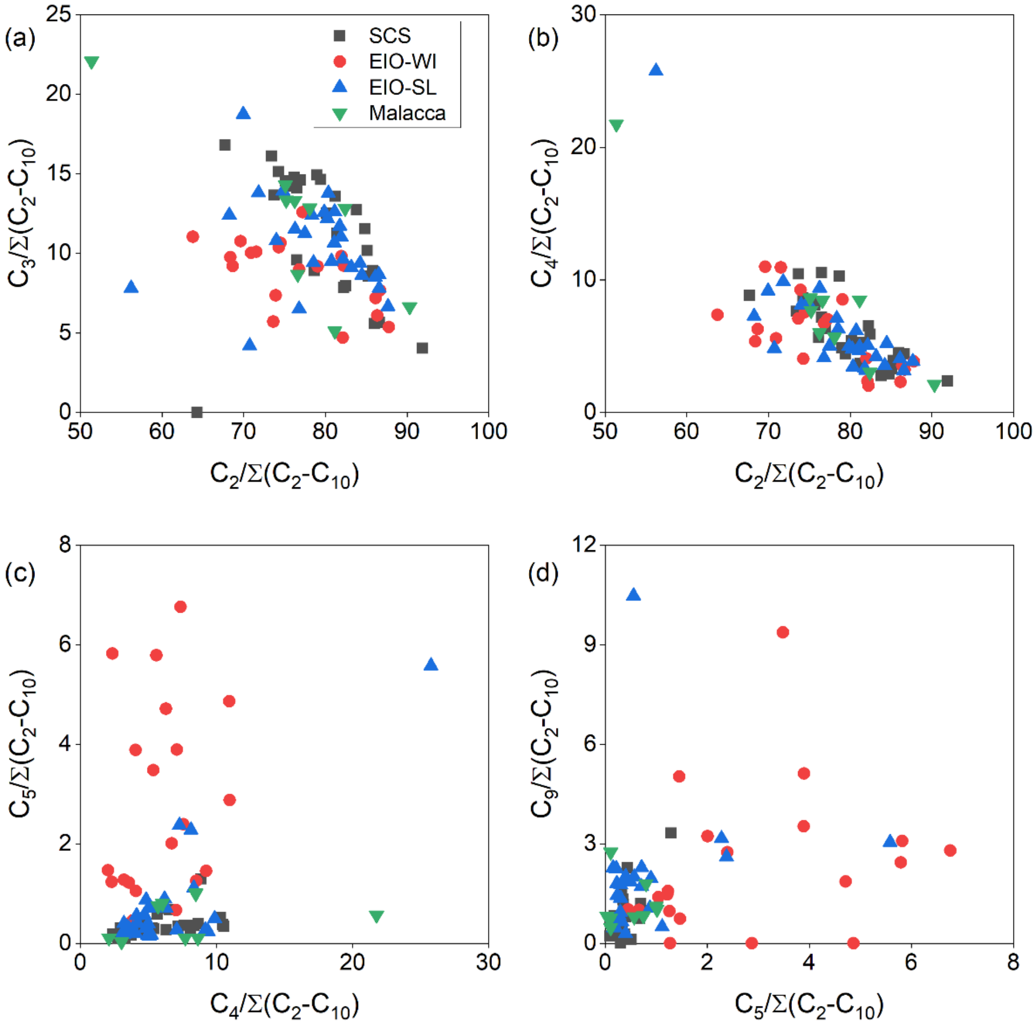


Figure S3. Scatterplots between the relative abundances of C_2 in their total aliphatic homologues (ΣC_2–C_{10}) with that of (a) malonic acid and (b) succinic acid. Likewise, scatterplots showing the relative abundances of C_5 in ΣC_2–C_{10} with those of (c) C_4 and (d) C_9 diacids in TSP samples collected during the NORC2015-10 cruise.

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Yang, L., Ray, M. B., and Liya, E. Y.: Photooxidation of dicarboxylic acids—Part II: Kinetics, intermediates and field observations, Atmospheric Environment, 42, 868-880, 2008.