Responses to Reviewer's Comments to

Zhang et al., *"Aircraft observations of water-soluble dicarboxylic acids in the aerosols over China"*

Anonymous Referee #1

The authors present a summary of airborne filter measurement data with a focus on dicarboxylic acids in aerosols over China. The topic of organic acid composition in aerosols is of interest to the atmospheric chemistry community since the organic fraction of particles is complex and uncertain, and requires improvements to be able to model their impacts better. The paper is written fairly well but requires some minor English editing (I point out a few suggested changes below for improving the language).
The tables and figures are appropriate. The title and abstract are also appropriate in terms of representing the contents of the manuscript.
The methods used are fine, and the results are informative and rich. The strength of the work includes the detection of so many organic acids that exceed the range of acids detected in some past studies relying on airborne measurements. The overall conclusions mostly repeat those in other studies though, which I hope the authors can address in their revisions. This study confirms that organic acids are generated
by secondary production mechanisms and that aqueous processing can be important, especially aloft. To strengthen the paper, I would suggest that the authors try to find something new in their data to push the state of understanding of organic acids forward as compared to repeating what has already been documented. The data generated are of high value as airborne diacid data are scarce, so it would be useful to have this work published. But before that happens, as noted above, it is requested that the authors narrow in better on what is novel in their dataset to highlight better in their text. This may be assisted by better consideration of what past work has shown and how this dataset can extend upon those past papers, some of which are highlighted below.

Response: we thank the reviewer for the nice summary of our paper and the positive comments. In the following responses, we will reply to each comment listed below individually.

Major Comments:
The authors should expand discussion on the potential influence of biomass burning on their measurements. When was biomass burning evident and how did this impact the organic acid data? Presumably the authors have reasonable tracers for biomass burning plumes.

Response: In the revised MS, we discussed the effects of biomass burning on diacids as follows. "Levoglucosan (1,6-Anhydro-β-D-glucopyranose) has been used as a source tracer for biomass burning (Liu et al., 2013;Fu et al., 2012). Levoglucosan shows a significant correlation with oxalic acid and also secondary organic aerosol (SOA) tracers (Figure 5),

indicating that that biomass burning is an important source of oxalic acid and SOA. It is interesting to note that levoglucosan was more abundant in spring than in summer. In addition, regression slope and correlation coefficient between oxalic acid and levoglucosan are higher in spring (i.e., slope: 2.7, r: 0.95) than in summer (i.e., slope: 1.7, r: 0.67), indicating that biomass-burning emissions play more important roles in spring than summer. Such higher values of slope of regression line and correlation coefficient were also found between levoglucosan and α/β-pinene- and β-caryophyllene-oxidation products, emphasizing an importance of springtime biomass burning. However, isoprene-oxidation products have a higher correlation coefficient with levoglucosan in summer than in spring, implying that biomass burning in summer is an important contributor of isoprene-derived SOA." Please see lines 338-350 in the revised MS.
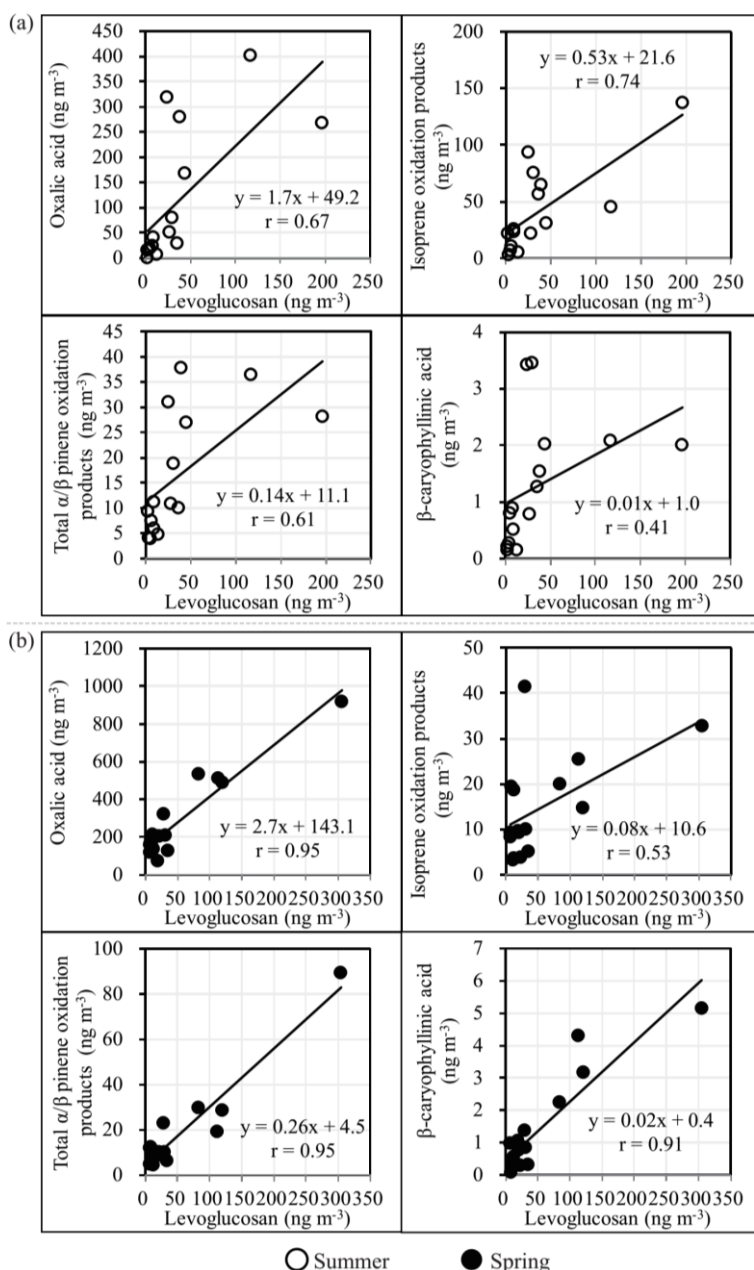
Figure R1. Linear relationship for the concentrations of levoglucosan with oxalic acid, isoprene SOA tracers, α/β-pinene SOA tracers and β-caryophyllene SOA tracer from the aircraft measurements over China during (a) summer and (b) spring.

In various places in the manuscript the authors refer to Free Troposphere (e.g., Line 285). They should make it clear what data and criteria they used to distinguish between FT and the lower mixing layer.

Response: To clarify it, we change "at high altitudes within FT to "at high altitudes within the lower/middle troposphere". Similarly, we made changes in other places. Such terms have also been used in previous studies (Fu et al., 2014;Wang et al., 2007).

Since denuders are not mentioned in the instrument description, the authors should comment on what impact the lack of using denuders have on the data. The authors should make note of what affect temperature effects would have on their data as during aircraft sampling there likely are differences in temperature between ambient air and their filters.

Response: In the revised MS, we added the following sentences; "The lack of using organic denuders may lead to a positive artifact (e.g., 10% of the organic carbon) by possible adsorption of gas-phase organic acids on the quartz filters (Cheng et al., 2009), but this will not affect our conclusions. Because air conditioning was not available in the aircraft, the ambient temperatures inside and outside the cabin should be similar, and thus potential adsorption of gaseous organic acids on quartz filter should be minimal."

Specific Comments: Page 1, Line 4: change 'organics' to 'organic'

Response: Done.

Page 2, Line 38-41: Diacids have also been measured in other areas such as deserts and this should be noted for the sake of completeness (example provided here):
Sorooshian, A., et al. (2012). Hygroscopic and chemical properties of aerosols collected near a copper smelter: Implications for public and environmental health, Environ. Sci. Technol., 46, 9473-9480.

Response: We have referenced this paper.

Page 2, Line 41: 'play an important role in. . .'

Response: Changed.

Page 3, Line 66-69: For completeness the authors should refer to the following other airborne studies: For 'Coastal marine stratocumulus and cumulus clouds over USA', add:

Wonaschuetz, A., et al. (2012). Aerosol and gas re-distribution by shallow cumulus clouds: an investigation using airborne measurements, J. Geophys. Res., 117, D17202, doi:10.1029/2012JD018089.

Prabhakar, G., et al. (2014). Sources of nitrate in stratocumulus cloud water: Airborne measurements during the 2011 E-PEACE and 2013 NiCE studies, Atmos. Environ., 97, 166-173, doi:10.1016/j.atmosenv.2014.08.019.

Measurements have been conducted over inland agricultural and urban areas in the western United States: Sorooshian, A., et al. (2015). Surface and airborne measurements of organosulfur and methanesulfonate over the western United States and coastal areas, J. Geophys. Res., 120, doi:10.1002/2015JD023822.

Response: These papers are now cited.

Line 98: 'for a series. . .'

Response: Changed.

Line 325-327: The discussion here can benefit from inclusion of past work showing how the relative amount of oxalate (versus total organic mass) increases with relative humidity based on airborne measurements [Sorooshian, A., et al. (2010). Constraining the contribution of organic acids and AMS m/z 44 to the organic aerosol budget: On the importance of meteorology, aerosol hygroscopicity, and region, Geophys. Res. Lett.,37, L21807, doi:10.1029/2010GL044951] and how water-soluble organics have been shown to be enhanced relative to the surface when humid conditions aloft [Duong, H. T., et al. (2011). Water-soluble organic aerosol in the Los Angeles Basin and outflow regions: Airborne and ground measurements during the 2010 CalNex field campaign, J. Geophys. Res., 116, D00V04, doi:10.1029/2011JD016674.].

Response: We acknowledge the reviewer's comments. Although we did not measure relative humidity in these campaigns, the references were added in the revised MS.

Supplement Table 1: For altitude, the authors should include a plus/minus standard deviation since it seems unlikely that the aircraft was level for that long of a period for each sample.
Response: The accuracy in the altitude is roughly ±10%. This point has been added in the revised MS.

Line 356: What do the authors mean by the word 'control'? This seems like a very strong word that may not be warranted here. Are these diacids the majority of the OA mass and, if so, can this be shown in the manuscript in a revision?

Response: We change "control" to "have important impacts on".

Table 2: The authors should make mention of the sample number involved with these correlation calculations somewhere in the table or caption.

Response: Samples numbers for calculations are included in the revised caption.

Anonymous Referee #2
Received and published: 29 February 2016
The manuscript by Zhang et al studied distributions of organic compounds obtained by aircraft measurements in China and argued that contribution of aqueous-phase photochemistry to SOA formation is significant using various correlation analyses. **Potentially this work will make an important contribution to SOA studies particularly in East Asia and be suitable for ACP readership.** But some of authors' arguments are confusing, misleading, and not clearly supported by evidence. Most of all, the organization is not effective. I highly recommend that authors should work on organization by bringing the LWC-oxalic acid analysis (currently in the end) to the front in Results and Discussion (Section 3) so that readers are clear about the main point of this manuscript is aqueous chemistry contribution to SOA. This will minimize confusions from paragraphs (Line 279-283, Line 283-285 and Line 291-299). Then, authors can discuss biogenic/anthropogenic influences on oxalic acid formation and aqueous chemistry. Provide biogenic/anthropogenic emission data if available. Provide NOx measurements, too for isoprene arguments. Take an advantage of referencing most recent papers. Below I provide comments. There are also numerous technical errors (e.g., grammatical errors, typos), which need to be corrected.

Response: We thank the reviewer for the nice summary of our paper and the positive comments. In the following we will respond to each comment listed below separately. In the revised MS, we moved the LWC-oxalic acid analysis (currently at the end) to the beginning of Results and Discussion section (Section 3). Further we included NOx data in the isoprene arguments, but we did not include biogenic/anthropogenic emission data because it is not available.

Line 38: Authors should clarify LMW. For example, is LWM less than 300? Or is a C5 diacid still LMW?

Response: In this paper, we measured diacids with carbon numbers from 2 to 11. To make it clearer, we remove "LMW" in the revised paper.

Line 41: LWM diacids -> Aerosols

Response: We changed the phrase to "As important components of aerosols, diacids …".
Line 43: contribute from -> contribute to the wide range from

Response: Changed.

Line 56: is -> are

Response: Changed.

Line 62-64: This is a modeling study of cloud chemistry. There is no evidence yet from lab or field studies supporting this argument. There should be more discussions. Authors may discuss the mechanism of isoprene photooxidation focusing on partitioning of water soluble photooxidation products into the aqueous phase leading to oxalic acid formation.

Response: We rephrased the sentence as "Indeed, from a model study it has been proposed that photochemical oxidation of isoprene and subsequent partitioning of water soluble photooxidation products into the aqueous phase is a predominant formation pathway of oxalic acid (Myriokefalitakis et al., 2011)."

Line 74: I don't see a verb in the sentence.

Response: We rephrased "maybe" to "may be".

Line 89: I am not clear about this. What are the examples of chemical constraints? And what more need to be considered?

Response: We changed "chemical constraints" to "chemical constraints (e.g., simultaneously measuring different types of organic aerosols such as diacids, ketoacids and α-dicarbonyls and SOA tracer compounds)".

Line 101: identified -> observed

Response: Changed.

Line 175-178: C5 and C6 diacids are the ozonolysis products in smog chamber studies. How does that support photooxidation (OH radical reaction or photolysis) of anthropogenic precursors? If cloud (photo)chemistry was involved, authors need to state that. Besides, authors should provide evidence (or reference) of higher oxidation capacity in the areas (or polluted areas) during the summer than winter.

Response: Although C5 and C6 diacids are the ozonolysis products in smog chamber studies, Pavuluri et al. (2015) recently proposed that C5 and C6 species are produced by photochemical processing of aqueous aerosols based on a laboratory experiment. In addition, C5 and C6 diacids have been used good tracers for anthropogenic sources in many studies (Kawamura and Bikkina, 2016). Using a global chemical transport model, the distributions of tropospheric OH over China show that tropospheric OH are higher in summer than in spring and winter (Shen and Wang, 2012;Su et al., 2012). These points have been added in the revised MS.

Line 188-200: OH reactions of water soluble organic compounds in the aqueous phase clearly produce malonic and succinic acid (Tan et al., EST, 2009). Authors should include this in their discussion. How does aqueous photooxidation affect C3/C4?

Response: In the revised MS, we added the following discussion, which reads as "In addition, C3 and C4 diacids can be formed by OH reactions of water soluble organic compounds such as glyoxal (Tan et al., 2009) and C3/C4 ratios gradually decrease with the reaction time (Pavuluri et al., 2015). The lower C3/C4 ratios in summer indicate that diacid aerosols are relatively fresh but will be subjected to more atmospheric aging than in other seasons due to increased OH concentrations and solar radiation." These points are added in the revised version.

Line 219-222: It seems this statement contradicts the previous statement (Line 184-186).

Response: This statement means that produced SOA is mostly fresh without intensive aging as evidenced by high M/F and low C3/C4 ratios. If SOA is intensively aged, M and C4 will be transformed to F or degraded to C3, respectively, but it is not observed in our study.

Line 221: Does "the low troposphere" means the ground level?

Response: We rephrased "the low troposphere" to "the lower/middle troposphere", to be consistent with previous terms used in the same campaign (Fu et al., 2014;Wang et al., 2007).

Line 232-233: Again, provide evidence or reference.

Response: References are added (Shen and Wang, 2012;Su et al., 2012).

Line 245: I would note that C2 is oxalic acid. Let readers know that Cn is n-numbered carbon diacid somewhere in the text.

Response: Following the comment, we rephrased the sentence.

Line 248-250: Remove wC2 if you mean HCO-COOH is glyoxylic acid, which is an oxidation product of pyruvic acid, glyoxal, and methylglyoxal. Also reference Lim et al., ACP 2013, which show a full mechanism for aqueous OH reactions.

Response: We revised the MS by taking the comment.

Line 252-255: I doubt this is true. Oxalic acid is the most dominant product for glyoxal with the high yield (Tan et al. EST, 2009; Lim et al., ACP, 2010). But it is not for methylglyoxal. So, the given correlation analysis cannot tell whether C2 is biogenic.

Response: Yes, we agree with the comment. We change the sentences as "We found that the correlation coefficient between Gly and C_2 is higher than that for MeGly and C_2 in winter and spring samples, being consistent with the fact that oxalic acid is the dominant product of glyoxal with the high yield but not for methylglyoxal (Tan et al., 2009; Lim et al., 2010)."

Line 256-259: The same goes here. Is there any evidence support that winter is more anthropogenically influenced (e.g., seasonal emission inventory)?

Response: We do not have emission inventory data, but a recent study reveals that air pollutants such as SO_2, NO_2, PM2.5 and PM10 are higher in winter than in summer and these pollutants are mostly from anthropogenic emissions (Zhang and Cao, 2015). This is now included.

Line 267-268: 2-methyltetrols are also isoprene SOA tracers. This means oxalic acid correlated with some of isoprene SOA tracers, not all.

Response: we rephrased the sentence as "Oxalic acid shows a strong positive correlation with *two specific* isoprene-derived SOA tracers such as 2-methylglyceric acid (2-MGA) and C_5-alkene triols (cis-2-methyl-1,3,4-trihydroxy-1-butene,3-methyl-2,3,4-trihydroxy-1-butene plus trans-2-methyl-1,3,4-trihydroxy-1-butene)."

Line 269: Are you sure there are diepoxy derivatives from isoprene? None of Paulot et al. Science, 2009 and Surratt et al. PNAS, 2010 reports that. If it is a typo, then change it to epoxy derivatives.

Response: It should be epoxy derivatives. We rephrased it as epoxy derivatives.

Line 270: further oxidation -> further gas-phase oxidation. There is no aqueous chemistry involved here.

Response: Corrected.

Line 272-274: NOx is critical in isoprene-OH reactions. In the presence of NOx, methacrolein and MVK form. In the absence of NOx, ISOPOOH forms and further ISOPOOH reactions produce IEPOX. To support your conclusion, you should provide NOx measurements.

Response: Overall, tropospheric atmosphere over China was characterized with relative high NOx concentrations. We rephrased the sentence as "Such a good correlation between 2-MGA and oxalic acid could demonstrate that oxalic acid has a very close link with the higher-generation products of isoprene in the presence of relatively high NO_x (i.e., NO_x averaged to 6.6±4.0 ppbv in summer and 3.9±3.3 ppbv), which could serve as precursors of oxalic acid over China."

Line 279-283: This statement is confusing. Are you saying oxalic acid is formed via gas-phase oxidation without aqueous reactions and lifted up to FT? But, there is no evidence of oxalic acid formation from gas-phase oxidation of isoprene or monoterpene. Besides, recent lab and field studies suggest that IEPOX contributes to SOA via aqueous chemistry (Nguyen et al. ACP, 2010; Budisulistiorini et al., ACP 2015; Pye et al., EST, 2013).
Response: We modified the sentence as "Based on the consistent good correlations of oxalic acid with SOA tracers derived from isoprene, monoterpene and β-caryophyllene, we propose

that a large fraction of oxalic acid in the lower/middle troposphere over China is of secondary origin, i.e., via aqueous chemistry."

Line 281: What is the boundary layer height? Is this 2 km, the lower FT?

Response: The boundary layer height was not measured. We rephrased "the boundary layer height" to "the lower/middle troposphere" to be consistent with terms used in this and previous study.

Line 283-285: It is difficult to conclude like this unless authors provide compelling evidence of aqueous chemistry leading to oxalic acid.

Response: Based on the consistent good correlations of oxalic acid with specific SOA tracers in aerosols, we could propose that oxalic acid is of secondary origin. We rephrased "should" to "may".

Line 291-299: These statements are also confusing. Why should oxalic acid be considered for SOA? Note that oxalic acid itself is not SOA due to high vapor pressure. I would agree if you argue that oxalic acid is evidence of aqueous chemistry. Then, you need to discuss how water soluble compounds formed from biogenic and anthropogenic sources; how they partition into wet aerosols or cloud waters; and how OH radicals formed and initiated aqueous-phase photooxidation.

Response: Although oxalic acid has relatively high vapor pressure, it has been observed as the most abundant individual organic compounds in aerosols (Kawamura and Bikkina, 2016). Our study together with many previous studies have revealed that oxalic acid is mostly from aqueous-phase production and is therefore of secondary origin (Myriokefalitakis et al., 2011). In addition, oxalic acid may partly exist as hydrated and/or salt forms in aerosols. Therefore, it is important to consider oxalic acid or oxalate as important SOA tracers. Please see lines 332-337 in the revised MS.

Besides, you mentioned C5 and C6 are from anthropogenic sources. But this chemistry is initiated by ozone and not related to aqueous chemistry. How is including this chemistry likely to reduce the discrepancy between model predictions and measurements of OA?

Response: We removed the following sentences "~~Inclusion of oxalic acid (and also other LWM diacids) as major products from atmospheric oxidation of biogenic (and also anthropogenic) VOCs may partially reduce the discrepancy between modeled and observed tropospheric OA during the ACE-Asia campaign , although further studies are still required to investigate other SOA compounds (e.g., oligomeric components) produced from anthropogenic and biogenic VOCs in the reactions to fully understand the associated formation pathway and mechanism~~".

Line 308: Do you mean higher altitude at low FT?

Response: We rephrased it as "in the upper troposphere (~2 km)."

Line 314: Specify "other species." Can they also provide evidence of aqueous chemistry like oxalic acid.

Response: This sentence has been removed in the revised MS.

References:

Cheng, Y., He, K. B., Duan, F. K., Zheng, M., Ma, Y. L., and Tan, J. H.: Positive sampling artifact of carbonaceous aerosols and its influence on the thermal-optical split of OC/EC, Atmos. Chem. Phys., 9, 7243-7256, 2009.

Fu, P., Kawamura, K., Chen, J., Li, J., Sun, Y., Liu, Y., Tachibana, E., Aggarwal, S., Okuzawa, K., and Tanimoto, H.: Diurnal variations of organic molecular tracers and stable carbon isotopic composition in atmospheric aerosols over Mt. Tai in the North China Plain: an influence of biomass burning, Atmos. Chem. Phys., 12, 8359-8375, 2012.

Fu, P. Q., Kawamura, K., Cheng, Y. F., Hatakeyama, S., Takami, A., Li, H., and Wang, W.: Aircraft measurements of polar organic tracer compounds in tropospheric particles (PM10) over central China, Atmos. Chem. Phys., 14, 4185-4199, 2014.

Kawamura, K., and Bikkina, S.: A review of dicarboxylic acids and related compounds in atmospheric aerosols: Molecular distributions, sources and transformation, Atmos. Res., 170, 140-160, 2016.

Liu, D., Li, J., Zhang, Y., Xu, Y., Liu, X., Ding, P., Shen, C., Chen, Y., Tian, C., and Zhang, G.: The use of levoglucosan and radiocarbon for source apportionment of $PM_{2.5}$ carbonaceous aerosols at a background site in East China, Environ. Sci. Technol., 47, 10454-10461, 2013.

Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A., and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study, Atmos. Chem. Phys., 11, 5761-5782, 2011.

Pavuluri, C. M., Kawamura, K., Mihalopoulos, N., and Swaminathan, T.: Laboratory photochemical processing of aqueous aerosols: formation and degradation of dicarboxylic acids, oxocarboxylic acids and α-dicarbonyls, Atmos. Chem. Phys., 15, 7999-8012, 2015.

Shen, L., and Wang, Y.: Changes in tropospheric ozone levels over the Three Representative Regions of China observed from space by the Tropospheric Emission Spectrometer (TES), 2005–2010, Chin. Sci. Bull., 57, 2865-2871, 2012.

Su, M., Lin, Y., Fan, X., Peng, L., and Zhao, C.: Impacts of global emissions of CO, NO x, and CH 4 on China tropospheric hydroxyl free radicals, Adv. Atmos. Sci., 29, 838-854, 2012.

Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Effects of Precursor Concentration and Acidic Sulfate in Aqueous Glyoxal−OH Radical Oxidation and Implications for Secondary Organic Aerosol, Environ. Sci. Technol., 43, 8105-8112, 2009.

Wang, G. H., Kawamura, K., Hatakeyama, S., Takami, A., Li, H., and Wang, W.: Aircraft measurement of organic aerosols over China, Environ. Sci. Technol., 41, 3115-3120, 2007.

Zhang, Y.-L., and Cao, F.: Fine particulate matter (PM2.5) in China at a city level, Scientific Reports, 5, 14884, 2015.

1   **Aircraft observations of water-soluble dicarboxylic acids in the aerosols over**

2   **China**

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Abstract

Vertical profiles of ~~low molecular weight~~ dicarboxylic acids, related organic compounds and SOA tracer compounds in particle phase have not yet been simultaneously explored in East Asia, although there is growing evidence that aqueous phase oxidation of volatile organic compounds may be responsible for the elevated organic aerosols (OA) in the ~~free~~ troposphere. Here, we found consistently good correlation of oxalic acid, the most abundant individual organic compounds in aerosols ~~s~~ globally, with its precursors as well as biogenic-derived secondary OA (SOA) compounds in Chinese tropospheric aerosols by aircraft measurements. Anthropogenically derived dicarboxylic acids (i.e., C_5 and C_6 diacids) at high altitudes were 4-20 times higher than those from surface measurements and even occasionally dominant over oxalic acid at altitude higher than 2 km, which is in contrast to the predominance of oxalic acid previously reported globally including the tropospheric and surface aerosols. This indicates an enhancement of tropospheric SOA formation from anthropogenic precursors. Furthermore, oxalic acid-to-sulfate ratio maximized at altitude of ~2 km, explaining aqueous-phase SOA production that was supported by good correlations with predicted liquid water content, organic carbon and biogenic SOA tracers. These results demonstrate that elevated oxalic acid and related SOA compounds from both the anthropogenic and biogenic sources may substantially contribute to tropospheric OA burden over polluted regions of China, implying aerosol-associated climate effects and intercontinental transport.

1 Introduction

~~Low molecular weight (LMW)~~Water-soluble dicarboxylic acids (diacids), one of the most abundant organic aerosol (OA) constituents, have been reported in the marine (Kawamura and Sakaguchi, 1999), remote (Kawamura et al., 1996), desert (Sorooshian et al., 2012), mountainous, rural, semi-urban, and urban atmosphere (Ho et al., 2007). ~~LMW diacids~~As important components of aerosols, diacids play an important role~~s~~ in Earth's climate by directly scattering sunlight or indirectly by enhancing the ability of OA to act as cloud condensation

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44 nuclei (CCN) (Kumar et al., 2003). They can contribute to wide ranges from a few percent of

45 the water-soluble mass (Sorooshian et al., 2007b), which could serve as tracers for the

46 atmospheric processing of water-soluble OA (Ervens et al., 2011), to more than 10% of organic

47 carbon (OC) in the remote marine atmosphere (Kawamura and Sakaguchi, 1999).

48 LMW diacids in aerosols may be directly emitted from fossil fuel combustion (e.g.

49 vehicle exhaust) (Kawamura and Kaplan, 1987), biomass burning (Narukawa et al., 1999) and

50 cooking emissions (Rogge et al., 1991). They can also be formed by degradation from

51 unsaturated fatty acids (Kawamura et al., 1996) and cyclic alkenes (Hatakeyama et al., 1987).

52 Laboratory studies have provided direct experimental evidence that stepwise aqueous oxidation

53 of relatively longer-chain (n) dicarboxylic acids can yield the corresponding short-chain (n-1)

54 dicarboxylic acids (Enami et al., 2015). In addition, in-cloud and below-cloud measurements

55 as well as other field measurements have revealed that aqueous-phase oxidation of volatile

56 organic compounds (VOCs) and intermediates such as glyoxal (Gly), methylglyoxal (MeGly)

57 and pyruvic acid (Pyr) in wet aerosols or clouds and the subsequent gas-particle partitioning

58 areis more important pathway for the production of small diacids such as oxalic and malonic

59 acids (Lim et al., 2013;Carlton et al., 2007;Lim et al., 2005;Carlton et al., 2006;Yu et al.,

60 2005;Sorooshian et al., 2007b;Sorooshian et al., 2006;Zhang et al., 2016). Oxalic acid (C_2) is

61 the most abundant diacid with concentrations ranging from a few ng m^{-3} in remote locations

62 (Kawamura et al., 1996) to hundreds or even up to one thousand ng m^{-3} in urban regions (Ho

63 et al., 2007) and highly forested regions (Falkovich et al., 2005). Indeed, from a model study it

64 has been proposed that photochemical oxidation of isoprene and subsequent partitioning of

65 water soluble photooxidation products into the aqueous phase is a predominant formation

66 pathway of oxalic acid (Myriokefalitakis et al., 2011). Indeed, it has been reported that

67 photochemical oxidation of isoprene is a predominant formation pathway of oxalic acid

68 (Myriokefalitakis et al., 2011).

69 Most of the previous studies of diacids and other organic compounds in aerosols have

70 been conducted at ground surface; however, only a few aircraft observations that have been

71   conducted over the arctic region (Talbot et al., 1992), the western North Pacific (Narukawa et

72   al., 1999), the western rim of the Pacific Ocean (Kawamura et al., 2003), the coastal marine

73   stratocumulus and cumulus clouds over USA (Crahan et al., 2004;Sorooshian et al.,

74   2013;Sorooshian et al., 2007a;Wonaschuetz et al., 2012;Prabhakar et al., 2014) and over inland

75   agricultural and urban areas in the western United States (Sorooshian et al., 2015). These aircraft

76   experiments have revealed that water-soluble diacids may be produced by the photochemical

77   oxidation of anthropogenic organic compounds in the atmosphere and thus play an important

78   role in controlling the chemical and physical properties of OA in the troposphere. However, the

79   evidence of secondary production of LWM diacids (i.e., oxalic acid) in tropospheric aerosols

80   may be not enough due to the lack of dataset from simultaneous measurements of their possible

81   precursors and/or intermediates such as particle-phase glyoxal (Gly), methylglyoxal (MeGly),

82   pyruvic acid (Pyr) and glyoxylic acid (ωC_2) as well as other secondary organic aerosol (SOA)

83   compounds from photochemical oxidation of VOCs such as isoprene and monoterpenes in the

84   aerosols collected from aircraft campaigns.

85   East Asia is one of the most important source regions of OA (Zhang et al., 2007), and

86   this is especially true for China due to the rapid urbanization, industrialization and energy

87   consumption (Huang et al., 2014;Zhang et al., 2015a;Zhang and Cao, 2015). Elevated OA were

88   found in the free troposphere (FT) from ACE-Asia aircraft observations, exceeding model-

89   predicted organic aerosols by a factor of 10-100 (Heald et al., 2011;Heald et al., 2005;Henze

90   and Seinfeld, 2006). There is growing evidence that SOA formation from aqueous phase

91   processing of VOCs, especially from isoprene may partially explain the missing OA in the

92   troposphere over East Asia (Heald et al., 2011;Heald et al., 2005;Henze and Seinfeld, 2006),

93   however, vertical profiles of LWM diacids, related organic compounds (i.e., ketoacids and α-

94   dicarbonyls) and SOA tracer compounds in particle phase have not yet been simultaneously

95   analyzed in this region. Additional chemical constraints (e.g. simultaneously measuring

96   different types of organic aerosols such as diacids, ketoacids and α-dicarbonyls and SOA tracer

97   compounds) are urgently required to investigate the importance of SOA formation pathway to

98   the global/regional budget of OA. Our previous studies have reported the molecular

99   composition of primary organic aerosols (POA) including n-alkanes, fatty acids, sugars, and

100 polycyclic aromatic hydrocarbons (PAHs) as well as biogenic SOA tracers in aerosol particles

101 over China (Wang et al., 2007;Fu et al., 2014). However, chemical composition and molecular

102 distribution of LMW diacids have never been reported by aircraft measurements over mainland

103 and coastal China, although only limited studies have been conducted on their spatial

104 distributions based ground observations (Ho et al., 2007).

105   In this study, we have collected aerosol samples over coastal to inland China using

106 aircraft during spring, summer and winter. The samples were analyzed for a -series of LWM

107 diacids and related compounds as well as SOA tracer compounds to investigate the vertical

108 profiles, possible sources and formation pathways of LWM diacids and related organic

109 compounds in the polluted troposphere over China. In light of these analyses, we ~~identified~~

110 observed that production of oxalic acid and related compounds from anthropogenic and

111 biogenic precursors is enhanced at high altitudes in the troposphere.

112 **2 Materials and Methods**

113 **2.1 Aircraft Campaigns**

114   Aircraft measurements were carried out over the coastal East China Sea in winter

115 (12/25/2002−01/06/2003, n=18) and inland China during summer (08/08/2003−09/13/2003,

116 n=14) and spring (05/19/2004−06/10/2004, n=16) using Yun-12 and Yun-5 airplanes as

117 described elsewhere(Wang et al., 2007;Fu et al., 2014) . The sampling heights were from 500

118 m to 3000 m (with uncertainty of around 10%) above ground level across many major cities

119 such as Changzhou, Nanjing, Hefei, Wuhan, Chongqing and Chengdu for inland aerosol

120 samples as well as Wenzhou, Ningbo, Shanghai, Changzhou, Qingdao and Dalian for coastal

121 aerosol samples. The detailed flight tracks and flight information are shown in Figure 1 and

122 Table S1 (see Supporting Information). PM$_{2.5}$ aerosols were collected on pre-heated quartz

123 fiber filter (diameter of 90 mm) using a medium-volume air sampler (Beijing Geological

124 Instrument Factory, China). Aerosol samples were collected for the sampling period from ca.

125 80 min. to two hours. Air was taken via an inlet installed below the cabin of the aircraft at a

126 flow rate of 78 L/min. The lack of using organic denuders may lead to a positive artifact (e.g.,

127 10% of the organic carbon) by possible adsorption of gas-phase organic acids on the quartz

128 filters (Cheng et al., 2009), but this will not affect our conclusions. Because air conditioning

129 was not available in the aircraft, the ambient temperatures inside and outside the cabin should

130 be similar, and thus potential adsorption of gaseous organic acids on quartz filter should be

131 minimal.

132 **2.2 Measurement of LMW diacids**

133   LMW diacids and related organic compounds such as ω-oxocarboxylic acids (or

134 oxoacids), pyruvic acid and α-dicarbonyls were determined as described elsewhere (Kawamura

135 and Ikushima, 1993;Ho et al., 2010). Briefly, the sample and blank filters were extracted with

136 organic free ultrapure water (10 ml × 3) in a glass vial for 10 min. To remove insoluble particles

137 and filter debris, the extracts were passed through a Pasteur pipette packed with quartz wool.

138 The combined extracts were concentrated using a rotary evaporator under a vacuum and then

139 further concentrated using a nitrogen blow-down system. The concentrated extracts were

140 reacted with 14% BF_3/n-butanol to derive carboxyl group to dibutyl ester and oxo group to

141 dibutoxy acetals.

142   The derivatives were extracted with n-hexane, concentrated to near dryness, dissolved

143 with n-hexane in 1.5 ml glass vials. The samples were finally determined using a gas

144 chromatography (GC, HP6980) with a split/splitless injection, fused silica capillary column

145 (HP-5, 0.2 mm i.d. x 25 m long x 0.52 µm film thickness) and a flame ionization detector.

146 Identification of the compounds was performed by GC retention times with those of authentic

147 standards and GC/mass spectrometry analyses. Recoveries of authentic standards spiked to a

148 pre-heated quartz fiber filter were generally better than 85% for all organic compound identified

149 except for oxalic acid (78%), pyruvic acid (72%), and methylglyoxal (55%). Duplicate analyses

17

150 of filter samples from other sites indicated that analytical errors are smaller than 15%. During

151 the aircraft campaigns, field blank filters were mounted onto the sampler for seconds without

152 pumping. Blank and sample filters were placed individually in a clean (pre-combusted at 450

153 °C for 6 h) glass jar sealed with a Teflon-lined screw cap, transported to the laboratory, and

154 stored at -20 °C prior to analysis (Wang et al., 2007).

155 Small peaks of oxalic, malonic and glyoxylic acids were found in the field and lab

156 blanks, but they were smaller than 10% of the real samples. The concentrations reported here

157 are all corrected for the field blanks but not for the recoveries. The method of SOA tracers

158 measurement was described elsewhere (Fu et al., 2014) .

159 **2.3 Measurements of EC and OC**

160 The concentrations of organic carbon (OC) and elemental carbon (EC) were measured

161 with thermal-optical transmittance method by OC/EC Carbon Aerosol Analyzer (Sunset

162 Laboratory Inc., USA) following the IMPROVE protocol (Chow et al., 2004). All the analyses

163 of the filter samples were completed in 2006.

164 **2.4 Estimation of liquid water content and aerosol acidity**

165 Liquid water content (LWC) and aerosol acidity were predicted by ISORROPIA II,

166 which is a thermodynamic equilibrium model with robust and rapid convergence for all aerosol

167 types (Fountoukis and Nenes, 2007). Measured concentrations of water-soluble inorganic ions,

168 ambient temperature and relative humility were used as input.

169 **3 Results and discussion**

170 **3.1 Concentrations and molecular distributions**

171 Total concentrations of LWM diacids and related compounds quantified in the inland

172 aircraft $PM_{2.5}$ (i.e., particulate matter with a diameter smaller than 2.5 µm) are 730±328 and

173 586±457 ng m^{-3} during summer and spring, respectively, while in the coastal aerosols, the

174   average concentration is 254±209 ng m^{-3} in winter (Table 1). It is of great interest to note that

175   the concentrations of diacids in the troposphereFT over the Arctic and North Pacific are

176   generally much lower than those reported at ground levels (Kawamura et al., 1996;Kawamura

177   and Sakaguchi, 1999); however, the concentrations in the troposphere over mainland China are

178   within the range of or even higher than those reported at ground levels in major cities (Ho et

179   al., 2007;Kawamura and Ikushima, 1993). Due to the enhanced anthropogenic emissions,

180   concentrations of POA (i.e., n-alkanes, fatty acids, sugars, lignin and resin products, sterols,

181   PAHs, and phthalic acids) are higher in winter than those in summer and spring (Wang et al.,

182   2007). In contrast, the concentrations of diacids in summer and spring are 2-15 times higher

183   than those in winter, indicating that these compounds are mostly of secondary origin via the

184   oxidation of their gaseous precursors such as isoprene and α/β-pinene (Kanakidou et al.,

185   2005;Carlton et al., 2006;Carlton et al., 2007;Carlton et al., 2009;Ervens et al., 2011) as

186   discussed below.

187   Molecular distributions of diacids (C$_n$ is n-numbered carbon diacid) in our study are

188   generally characterized by the predominance of oxalic acid (C$_2$) followed by succinic (C$_4$) and

189   malonic (C$_3$) acids during spring and winter, being consistent with previous findings obtained

190   in Chinese megacities (Ho et al., 2007) (Figure 2a). However, in many summer samples

191   collected at height of above 2 km, we found the predominance of glutaric (C$_5$) and adipic (C$_6$)

192   acids (see Figure 2b), which are the major organic compounds produced by the oxidation of

193   anthropogenic cyclohexene and methylenecyclohexane (Hamilton et al., 2006;Muller et al.,

194   2007). Although C5 and C6 diacids are the ozonolysis products in smog chamber studies,

195   Pavuluri et al. (2015) recently proposed that C5 and C6 acids are produced by photochemical

196   processing of aqueous aerosols from a laboratory study. Such a molecular distribution has not

197   been reported for the free tropospheric and ground level aerosols (Hatakeyama et al.,

198   1987;Enami et al., 2015;Kawamura and Bikkina, 2016). In our measurements, the averaged

199   concentrations of C$_5$ and C$_6$ in summer are 159±79 ng m^{-3} and 93.9±23.2 ng m^{-3}, which are 4-

200   20 times higher than those in ground measurements in many megacities in China (Ho et al.,

19

201 2007), Tokyo (Kawamura and Yasui, 2005) and Los Angeles (Kawamura and Kaplan, 1987).

202 Such high abundances of C_5 and C_6 observed in summer imply an important formation pathway

203 associated with enhanced photochemical oxidation of anthropogenic precursors in the polluted

204 troposphere over China.

205 **3.2 C_3 (C_2) to C_4 ratio**

206 The malonic to succinic acid (C_3/C_4) ratios can provide information on source,

207 formation pathways and photochemical aging of organic aerosols. C_3/C_4 ratios in aerosols

208 derived from vehicular exhausts (i.e., 0.25–0.44, av. 0.35) (Kawamura and Kaplan, 1987) have

209 lower values than those in ambient aerosols from Tokyo (i.e., 0.56–2.9, av. 1.6) (Kawamura

210 and Ikushima, 1993) and China's megacities (i.e., 0.6–1.1, average 0.74) (Ho et al., 2007). In

211 contrast, the ratios are substantially higher for aged aerosols because C_3 is more produced by

212 photochemical processing of C_4 (Kawamura and Ikushima, 1993). Actually, higher C_3/C_4 ratios

213 are observed for remote marine aerosols from the North Pacific including tropic (range: 1–11,

214 av. 3.9) which are subjected to extensive aging during the long-range atmospheric transport

215 (Kawamura and Sakaguchi, 1999). In this study, C_3/C_4 ratios are 0.5±0.4 in summer, 0.9±0.1

216 in spring (Table 1), and 0.7±0.2 in winter, apparently smaller than those in aerosols affected by

217 atmospheric aging, but similar to that of urban aerosols in China (i.e., 0.9 in summer and 0.6 in

218 winter) (Ho et al., 2007). In addition, C3 and C4 diacids can be formed by OH reactions of

219 water soluble organic compounds such as glyoxal (Tan et al., 2009) and C3/C4 ratios gradually

220 decrease with the reaction time (Pavuluri et al., 2015). The lower C3/C4 ratios in summer

221 indicate that diacid aerosols are relatively fresh but will be subjected to more atmospheric aging

222 than in other seasons due to increasing OH concentrations and solar radiation.

223 C_2/C_4 ratios (2.0 in summer, 4.6 in spring and 4.6 in winter) in our study are found to

224 be much smaller than those from ground observations in China during summer (inland cities in

225 summer: av. 7.1) and winter (coastal cities in winter: av. 7.9). The lower C_2/C_4 and C_3/C_4 ratios

226 could be also resulting from degradation of C_2 and C_3 in high altitudes due to increased solar

227 radiation. However, no strong correlation ($p>0.05$) is found between C_2/C_4 (and C_3/C_4) and

228 sampling altitude although solar radiation is expected to increase with increasing altitudes.

229 These results suggest that the degradation of higher homologous diacids (i.e., C_4) is not an

230 important pathway for the production of tropospheric C_2 and C_3 in China, and primary fossil-

231 fuel emissions and/or secondary production from other precursors are major formation

232 pathways of these small diacids (i.e., C_2, C_3 and C_4).

233 3.3 Cis/trans ratio

234   It has been revealed that maleic acid (M, *cis* configuration) is produced by

235 photochemical oxidation of anthropogenic aromatic hydrocarbons such as benzene and toluene,

236 which is predominant over fumaric acid (F, *trans* configuration) (Sempere and Kawamura,

237 1996). M can be photo-isomerized to its *trans* isomer (*F)* in the atmosphere under solar

238 radiation. M/F ratios (4.9, 4.5 and 6.8 for summer, spring and winter, respectively) are much

239 higher in the present study than those reported in marine region (0.1-1.5) (Fu et al., 2013) and

240 Chinese megacities at ground levels (2.0 and 2.2 for summer and winter, respectively) (Ho et

241 al., 2007). This indicates that only a small fraction of maleic acid is isomerized to fumaric acid

242 by photochemical transformation and thus SOA produced from anthropogenic emissions in the

243 lower/middle troposphere in China is mostly fresh without substantially photochemical

244 processing (Cong et al., 2015).

245 3.4 C_5 (C_6) to C_9 diacid ratio

246   C_6 (or C_5) to azelaic acid (C_9) ratio (i.e., C_6/C_9 or C_5/C_9) is often used as an indicator

247 of relative contribution from anthropogenic and biogenic sources to OA (Kawamura and Yasui,

248 2005). C_6/C_9 and C_5/C_9 ratios during the summer aircraft campaign are on average 17 and 28,

249 respectively, which are >15 times higher than those reported at the ground surface from major

250 Chinese cities (Ho et al., 2007;Wang et al., 2002). This comparison further supports that

251 anthropogenic sources are an important source of OA in the high altitudes over China. Taken

252 together with other possible SOA components (e.g., oligomers with MW > 250 Da) produced

during the oxidation of anthropogenic VOCs, our result implies that SOA formation plays an important role in OA budget in the troposphere especially during summer when atmospheric oxidation capacity is significantly enhanced (Shen and Wang, 2012;Su et al., 2012). It is important to note that the correlation coefficient of C_6 (or C_5) with C_2 during summer (r^2=0.39 or 0.49) is lower than that obtained in winter (r^2=0.76 or 0.59) and spring (r^2=0.95 or 0.96), suggesting that C_2 has a different formation pathway and/or its precursors are mostly from biogenic origins (i.e., isoprene) in summer.

3.5 Correlation of diacids with SOA tracers and biomass burning tracers

In the urban atmosphere, dicarboxylic acids can be emitted as primary particles from motor exhausts (Kawamura and Kaplan, 1987), biomass burning (Cong et al., 2015;Falkovich et al., 2005), and cooking emissions (Rogge et al., 1991). However, recent field, laboratory and model studies have demonstrated that aqueous-phase SOA formation from isoprene or other precursors photooxidation is a major formation pathway of LMW diacids (Myriokefalitakis et al., 2011;Carlton et al., 2006;Ervens et al., 2011). Furthermore, significant correlations (r>0.70, p<0.05) are obtained between C_2 and its possible precursors and intermediates such as glyoxylic acid (ωC_2), pyruvic acid (Pyr), glyoxal (Gly) and methylglyoxal (MeGly) in all three campaigns (Table 2). This demonstrates that C_2 is produced from its precursor compounds such as Pyr, Gly and, MeGly ~~and ωC₂~~ through the following formation pathways: ($CH_3COCOOH$, $HCO-CHO$, CH_3COCHO) → $HCO-COOH$ → $HOOC-COOH$ (Carlton et al., 2009;Carlton et al., 2007;Carlton et al., 2006;Lim et al., 2013). ~~Based on the GEOS-Chem Global 3-D chemical transport model, Gly may be derived from both biogenic and anthropogenic VOCs whereas MeGly is more specific to biogenic isoprene (Fu et al., 2008).~~ We found that the correlation coefficient between Gly and C_2 is higher than that between MeGly and C_2 for winter and spring samples, being consistent with the fact that oxalic acid is the dominant product of glyoxal with the high yield but not for methylglyoxal (Tan et al., 2009;Lim et al., 2010).Indeed, a good correlation (Figure 3) was found between predicted liquid water content with both OC and oxalic acid, indicating an important contribution from SOA formation via cloud processing

and/or aqueous-phase oxidation. Aqueous-phase production of oxalic acid and related compounds may increase the abundances of SOA at the middle troposphere (around 2 km in this study), as discussed below. With the GEOS-Chem model based on the Fu et al. (2008) scheme (Fu et al., 2008), aqueous-phase SOA has a pronounced enhancement in the lower free troposphere (2-6 km) (Heald et al., 2011), which may explain to some extent the elevated levels of oxalic acid around at ~2 km in altitude.

~~suggesting a substantial contribution of SOA formation from anthropogenic VOCs during these two seasons.~~

Similarly, C_2 also shows better correlations with both anthropogenic-derived SOA such as C_5 and C_6 for winter (r^2=0.76 or 0.59) and spring (r^2=0.95 or 0.96) samples than summer samples (r^2=0.39 or 0.49), further supporting that anthropogenic VOCs play a more important role in SOA formation than biogenic VOCs during winter and spring. A recent study reveals that air pollutants such as SO_2, NO_2, $PM_{2.5}$ and PM_{10} are higher in winter than in summer and spring and these air pollutants are mostly from anthropogenic emissions (Zhang and Cao, 2015). No significant correlation (r^2=0.28, p>0.05) is found between EC (i.e., a primary tracer for fossil fuel biomass combustion (Zhang et al., 2015b)) and C_2 in summer aerosols, whereas a good correlation is found in spring. These results indicate that primary emissions are not major sources of C_2 during summer, but their contribution may be more important in spring.

Oxalic acid shows a strong positive correlation with isoprene-derived SOA tracers such as 2-methylglyceric acid (2-MGA) and C_5-alkene triols (cis-2-methyl-1,3,4-trihydroxy-1-butene,3-methyl-2,3,4-trihydroxy-1-butene plus trans-2-methyl-1,3,4-trihydroxy-1-butene) (Figure ~~3~~4), but a very weak correlation (r^2 = 0.26, p>0.05) with 2-methyltetrols (2-methylthreitol and 2-methylerythritol). Previous studies have revealed that 2-methyltetrols could be formed through ~~di~~epoxy derivatives of isoprene through acid-catalyzed hydrolysis (Wang et al., 2005), whereas 2-MGA is produced by further gas-phase oxidation of its intermediates such as methacrolein and methacrylic acid from isoprene (Claeys et al.,

2004;Surratt et al., 2006). Such a good correlation between 2-MGA and oxalic acid could demonstrate that oxalic acid has a very close link with the higher-generation products of isoprene in the presence of relatively high NO_x (i.e., NO_x averaged to 6.6±4.0 ppbv in summer and 3.9±3.3 ppbv), which could serve as precursors of oxalic acid over China., which could serve as precursors of oxalic acid over China. Oxalic acid also significantly correlates with α/β-pinene-SOA tracers (i.e., pinonic, pinic, 3-hydroxyglutaric, and 3-methyl-1,2,3-butanetricarboxylic acid) and β-caryophyllene tracer (β-caryophyllinic acid, see Figure 43) (Jaoui et al., 2013).

Overall, both oxalic acid and SOA tracers are more abundant in summer than in spring, suggesting that production of these organics is associated with higher oxidation capacity, emission strength and solar radiation in summer. Based on the consistent good correlations of oxalic acid with SOA tracers derived from isoprene, monoterpene and β-caryophyllene, we propose that a large fraction of oxalic acid in the lower/middle troposphere detected within the atmospheric boundary layer over China is of secondary origin, i.e., via aqueous chemistry mostly via atmospheric oxidation of gaseous precursors uplifted aloft from ground surface. This study highlights that oxalic acid may should serve as an important tracer of SOA formation not only on the ground surface but also at high altitudes within the lower/middle troposphere FT. Therefore, the high abundances of LWM diacids (C_2-C_6) observed in this study imply an important contribution to the OA budget from SOA production from both biogenic and anthropogenic precursors emitted from the ground surface to high altitudes over inland China.

The observed total concentrations of oxalic acid and other LWM diacids identified in this study (Table 1) show the same magnitude as the levels of SOA (i.e., 299±173 ng m^{-3} in summer and 257±210 ng m^{-3} in spring) estimated by SOA-tracer methods (Fu et al., 2014). It should be noted that oxalic acid is not included in the traditional "SOA tracer method" (Kleindienst et al., 2007) and therefore SOA may be underestimated if SOA is calculated by this approach. Although oxalic acid has relatively high vapor pressure, it has been observed as

the most abundant individual organic compounds in aerosols (Kawamura and Bikkina, 2016). Our study together with many previous studies have revealed that oxalic acid is mostly from aqueous-phase production and is therefore of secondary origin (Myriokefalitakis et al., 2011). In addition, oxalic acid may partly exist as hydrated and/or salt forms in aerosols. Therefore, it is important to consider oxalic acid or oxalate as important SOA tracers.

Levoglucosan (1,6-Anhydro-β-D-glucopyranose) has been used as a source tracer for biomass burning (Liu et al., 2013;Fu et al., 2012). Levoglucosan shows a significant correlation with oxalic acid and also secondary organic aerosol (SOA) tracers (Figure 5), indicating that that biomass burning is an important source of oxalic acid and SOA. It is interesting to note that levoglucosan was more abundant in spring than in summer. In addition, regression slope and correlation coefficient between oxalic acid and levoglucosan are higher in spring (i.e., slope: 2.7, r: 0.95) than in summer (i.e., slope: 1.7, r: 0.67), indicating that biomass-burning emissions play more important roles in spring than summer. Such higher values of slope of regression line and correlation coefficient were also found between levoglucosan and α/β-pinene- and β-caryophyllene-oxidation products, emphasizing an importance of springtime biomass burning. However, isoprene-oxidation products have a higher correlation coefficient in summer than in spring, implying that biomass burning in summer is an important contributor of isoprene-derived SOA.

Inclusion of oxalic acid (and also other LWM diacids) as major products from atmospheric oxidation of biogenic (and also anthropogenic) VOCs may partially reduce the discrepancy between modeled and observed tropospheric OA during the ACE-Asia campaign , although further studies are still required to investigate other SOA compounds (e.g., oligomeric components) produced from anthropogenic and biogenic VOCs in the reactions to fully understand the associated formation pathway and mechanis**3.6 Vertical profiles of LWM-diacids**

358   As shown in Figure 64, the highest concentrations of oxalic acid and total diacids are

359   observed around at 2 km in altitude during summer with a sharp decrease toward 3 km.

360   However, during spring and winter, their concentrations decrease with increasing altitudes due

361   to the atmospheric dilution during upward transport. Much clear trends are observed in the

362   vertical profiles of oxalic acid normalized by anthropogenic tracers such as sulfate (SO_4^{2-}),

363   vanadium, and bulk OC. Interestingly, similar trends are also found in spring and winter

364   samples, but the trends are weaker, suggesting that a secondary production of oxalic acid is

365   largely enhanced ~~in summer~~during summer ~~at higher altitudes of~~ in the upper~~lower~~ troposphere

366   (~2 km). Similar vertical pattern has been also reported for biogenic SOA-tracers such as 2-

367   MGA, 3-HGA and MBTCA (3-methyl-1,2,3-butanetricarboxylic acid), but not for POA such

368   as biomass burning tracers (e.g., levoglucosan), fungal spore tracers (arabitol and mannitol),

369   sucrose, and trehalose (Fu et al., 2014). These results further demonstrate that oxalic acid is

370   mostly likely produced by secondary process in the troposphere.

371   Oxalic acid ~~and related organic species identified~~ in the high altitudes could not be

372   simply explained by uplifting transport of pre-existing SOA produced on the ground surface

373   because these SOA compounds relative to anthropogenic tracers such as SO_4^{2-}, vanadium, and

374   OC significantly increased with altitude as stated above. This finding suggests that in-situ SOA

375   production by the oxidation of VOCs lifted from ground surface substantially contributes to the

376   observed levels of oxalic acid and related species. Therefore, SOA formation in cloud or wet

377   aerosol via the oxidation of biogenic and anthropogenic VOCs may increase concentrations of

378   oxalic acid at higher altitudes in the ~~lower FT~~troposphere. There is growing evidence to support

379   of in-cloud formation of oxalic acid and related SOA. Many studies suggest that oxalic acid is

380   mostly produced via aqueous-phase oxidation of water-soluble organics such as glyoxal,

381   methylglyoxal, pyruvic acid and glyoxylic acid, which are oxidation intermediates of various

382   VOCs (Ervens et al., 2004;Carlton et al., 2006;Ervens et al., 2011). ~~Indeed, a good correlation~~

383   ~~(Figure 5) was found between predicted liquid water content with both OC and oxalic acid,~~

384   ~~indicating an important contribution from SOA formation via cloud processing and/or aqueous-~~

26

385 ~~phase oxidation. This formation pathway is also supported by the consistently good correlation~~
386 ~~among these species identified in our study as discussed previously. Aqueous-phase production~~
387 ~~of oxalic acid and related compounds may increase the abundances of SOA at the lower FT~~
388 ~~(around 2 km in this study). With the GEOS-Chem model based on the Fu et al. (2008) scheme~~
389 ~~(Fu et al., 2008), aqueous-phase SOA has a pronounced enhancement in the lower FT (2-6 km)~~
390 ~~(Heald et al., 2011), which may explain to some extent the elevated levels of oxalic acid around~~
391 ~~at ~2 km in altitude.~~

392 **4 Conclusions**

393   Based on three aircraft measurements over East Asia, this study demonstrates an
394 aqueous-phase mechanism for SOA productions of diacids in the troposphere following
395 correlation analysis of oxalic acid in tropospheric aerosols with other measured chemical
396 variables including its precursors and its intermediate as well as biogenic-derived SOA from
397 isoprene, monoterpenes and β-caryophyllene. In addition to biogenic-derived SOA compounds,
398 anthropogenic-derived dicarboxylic acids (e.g. C5 and C6 diacids) are 4-20 times higher than
399 those from ground measurements and even occasionally dominant over oxalic acid at altitudes
400 higher than 2 km in summer, which is in contrast to the predominance of oxalic acid previously
401 reported globally including the tropospheric and surface aerosols. The results suggest an
402 important formation pathway associated with enhanced photochemical oxidation of
403 anthropogenic precursors in the polluted troposphere over China. Their relative contribution of
404 anthropogenic and biogenic sources is subject to future studies. The combination of radiocarbon
405 (^{14}C) measurement of water-soluble organic carbon (WSOC) and specific SOA compounds
406 (e.g., oxalic acid) may provide better insights on biogenic and fossil sources of SOA (Zhang et
407 al., 2014;Zhang et al., 2015a;Noziere et al., 2015) .

408   The present study demonstrates that secondary formation of oxalic acid in aqueous
409 phase plays an important role in the SOA budget from the near surface to the lower FT (i.e., 2
410 km) over inland China, whereas dilution of pre-existing particles and VOCs, photochemical

411 decomposition and aerosol processing may decrease the levels of oxalic acid and related

412 compounds at higher altitudes (>2 km). Our findings also highlight that water-soluble LMW

413 diacids and other SOA components may ~~control~~ have important impacts on the chemical

414 compositions, physical properties and budget of OA in the polluted troposphere over China,

415 and thus significantly affect the regional/global climate and intercontinental transport

416 especially over the Pacific Ocean.

Acknowledgements

References

427 Carlton, A. G., Turpin, B. J., Lim, H. J., Altieri, K. E., and Seitzinger, S.: Link between

428 isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility

429 organic acids in clouds, Geophys. Res. Lett., 33, L06822, 2006.

430 Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H. J., and Ervens, B.:

431 Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous

432 photooxidation experiments, Atmos. Environ., 41, 7588-7602, 2007.

433 Carlton, A. G., Wiedinmyer, C., and Kroll, J. H.: A review of Secondary Organic Aerosol

434 (SOA) formation from isoprene, Atmos. Chem. Phys., 9, 4987-5005, 2009.

435 Cheng, Y., He, K. B., Duan, F. K., Zheng, M., Ma, Y. L., and Tan, J. H.: Positive sampling

436 artifact of carbonaceous aerosols and its influence on the thermal-optical split of OC/EC,

437 Atmos. Chem. Phys., 9, 7243-7256, 2009.

438 Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., Moosmüller, H., and Fung, K.:

439 Equivalence of elemental carbon by thermal/optical reflectance and transmittance with

440 different temperature protocols, Environ. Sci. Technol., 38, 4414-4422, 2004.

441   Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J.,

442   Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic

443   aerosols through photooxidation of isoprene, Science, 303, 1173-1176, 2004.

444   Cong, Z. Y., Kawamura, K., Kang, S. C., and Fu, P. Q.: Penetration of biomass-burning

445   emissions from South Asia through the Himalayas: new insights from atmospheric organic

446   acids, Scientific Reports, 5, 9580, 2015.

447   Crahan, K. K., Hegg, D., Covert, D. S., and Jonsson, H.: An exploration of aqueous oxalic

448   acid production in the coastal marine atmosphere, Atmos. Environ., 38, 3757-3764, 2004.

449   Enami, S., Hoffmann, M. R., and Colussi, A. J.: Stepwise Oxidation of Aqueous Dicarboxylic

450   Acids by Gas-Phase OH Radicals, J. Phys. Chem. Lett., 6, 527-534, 2015.

451   Ervens, B., Feingold, G., Frost, G. J., and Kreidenweis, S. M.: A modeling study of aqueous

452   production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass

453   production, J. Geophys. Res., 109, D15205, 2004.

454   Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud

455   droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies,

456   Atmos. Chem. Phys., 11, 11069-11102, 2011.

457   Falkovich, A. H., Graber, E. R., Schkolnik, G., Rudich, Y., Maenhaut, W., and Artaxo, P.:

458   Low molecular weight organic acids in aerosol particles from Rondonia, Brazil, during the

459   biomass-burning, transition and wet periods, Atmos. Chem. Phys., 5, 781-797, 2005.

460   Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic

461   equilibrium model for K+-Ca2+-Mg2+-Nh(4)(+)-Na+-SO42--NO3--Cl--H2O aerosols,

462   Atmos. Chem. Phys., 7, 4639-4659, 2007.

463   Fu, P., Kawamura, K., Chen, J., Li, J., Sun, Y., Liu, Y., Tachibana, E., Aggarwal, S.,

464   Okuzawa, K., and Tanimoto, H.: Diurnal variations of organic molecular tracers and stable

465   carbon isotopic composition in atmospheric aerosols over Mt. Tai in the North China Plain:

466   an influence of biomass burning, Atmos. Chem. Phys., 12, 8359-8375, 2012.

467   Fu, P., Kawamura, K., Usukura, K., and Miura, K.: Dicarboxylic acids, ketocarboxylic acids

468   and glyoxal in the marine aerosols collected during a round-the-world cruise, Mar. Chem.,

469   148, 22-32, 2013.

470   Fu, P. Q., Kawamura, K., Cheng, Y. F., Hatakeyama, S., Takami, A., Li, H., and Wang, W.:

471   Aircraft measurements of polar organic tracer compounds in tropospheric particles (PM10)

472   over central China, Atmos. Chem. Phys., 14, 4185-4199, 2014.

473   Fu, T. M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global

474   budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of

475   secondary organic aerosols, J. Geophys. Res., 113, D15303, 2008.

476   Hamilton, J. F., Lewis, A. C., Reynolds, J. C., Carpenter, L. J., and Lubben, A.: Investigating

477   the composition of organic aerosol resulting from cyclohexene ozonolysis: low molecular

478   weight and heterogeneous reaction products, Atmos. Chem. Phys., 6, 4973-4984, 2006.

479   Hatakeyama, S., Ohno, M., Weng, J. H., Takagi, H., and Akimoto, H.: Mechanism for the

480   Formation of Gaseous and Particulate Products from Ozone-Cycloalkene Reactions in Air,

481   Environ. Sci. Technol., 21, 52-57, 1987.

482   Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H.,

483   and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current

484   models, Geophys. Res. Lett., 32, L18809, 2005.

485   Heald, C. L., Coe, H., Jimenez, J. L., Weber, R. J., Bahreini, R., Middlebrook, A. M., Russell,

486   L. M., Jolleys, M., Fu, T. M., Allan, J. D., Bower, K. N., Capes, G., Crosier, J., Morgan, W.

487   T., Robinson, N. H., Williams, P. I., Cubison, M. J., DeCarlo, P. F., and Dunlea, E. J.:

488   Exploring the vertical profile of atmospheric organic aerosol: comparing 17 aircraft field

489   campaigns with a global model, Atmos. Chem. Phys., 11, 12673-12696, 2011.

490   Henze, D. K., and Seinfeld, J. H.: Global secondary organic aerosol from isoprene oxidation,

491   Geophys. Res. Lett., 33, L09812, 2006.

492   Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J., Chow, J. C., and Watson, J. G.:

493   Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China,

494   J. Geophys. Res., 112, D22S27, 2007.

495   Ho, K. F., Lee, S. C., Ho, S. S. H., Kawamura, K., Tachibana, E., Cheng, Y., and Zhu, T.:

496   Dicarboxylic acids, ketocarboxylic acids, alpha-dicarbonyls, fatty acids, and benzoic acid in

497   urban aerosols collected during the 2006 Campaign of Air Quality Research in Beijing

498   (CAREBeijing-2006), J. Geophys. Res., 115, 2010.

499   Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y., Daellenbach, K. R.,

500   Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A.,

501   Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis,

502   J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S.:

503   High secondary aerosol contribution to particulate pollution during haze events in China,

504   Nature, 514, 218-222, 2014.

505   Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M., and Offenberg, J. H.:

506   Secondary organic aerosol formation from the oxidation of a series of sesquiterpenes: alpha-

507   cedrene, beta-caryophyllene, alpha-humulene and alpha-farnesene with O-3, OH and NO3

508   radicals, Environ. Chem., 10, 178-193, 2013.

509   Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van

510   Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski,

511   Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K.,

512   Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a

513   review, Atmos. Chem. Phys., 5, 1053-1123, 2005.

514   Kawamura, K., and Kaplan, I. R.: Motor Exhaust Emissions as a Primary Source for

515   Dicarboxylic-Acids in Los-Angeles Ambient Air, Environ. Sci. Technol., 21, 105-110, 1987.

516   Kawamura, K., and Ikushima, K.: Seasonal-Changes in the Distribution of Dicarboxylic-

517   Acids in the Urban Atmosphere, Environ. Sci. Technol., 27, 2227-2235, 1993.

518   Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of

519   dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations,

520   Atmos. Environ., 30, 1709-1722, 1996.

521   Kawamura, K., and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids

522   in marine aerosols over the Pacific Ocean including tropics, J. Geophys. Res., 104, 3501-

523   3509, 1999.

524   Kawamura, K., Umemoto, N., Mochida, M., Bertram, T., Howell, S., and Huebert, B. J.:

525   Water-soluble dicarboxylic acids in the tropospheric aerosols collected over east Asia and

526   western North Pacific by ACE-Asia C-130 aircraft, J. Geophys. Res., 108, 2003.

527   Kawamura, K., and Yasui, O.: Diurnal changes in the distribution of dicarboxylic acids,

528   ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, Atmos. Environ., 39,

529   1945-1960, 2005.

530   Kawamura, K., and Bikkina, S.: A review of dicarboxylic acids and related compounds in

531   atmospheric aerosols: Molecular distributions, sources and transformation, Atmos. Res., 170,

532   140-160, 2016.

533   Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Lewis, C. W., Bhave, P. V.,

534   and Edney, E. O.: Estimates of the contributions of biogenic and anthropogenic hydrocarbons

535   to secondary organic aerosol at a southeastern US location, Atmos. Environ., 41, 8288-8300,

536   2007.

537   Kumar, P. P., Broekhuizen, K., and Abbatt, J. P. D.: Organic acids as cloud condensation

538   nuclei: Laboratory studies of highly soluble and insoluble species, Atmos. Chem. Phys., 3,

539   509-520, 2003.

540   Lim, H. J., Carlton, A. G., and Turpin, B. J.: Isoprene forms secondary organic aerosol

541   through cloud processing: Model simulations, Environ. Sci. Technol., 39, 4441-4446, 2005.

542   Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and

543   its role in secondary organic aerosol (SOA) formation, Atmos. Chem. Phys., 10, 10521-

544   10539, 2010.

545   Lim, Y. B., Tan, Y., and Turpin, B. J.: Chemical insights, explicit chemistry, and yields of

546   secondary organic aerosol from OH radical oxidation of methylglyoxal and glyoxal in the

547   aqueous phase, Atmos. Chem. Phys., 13, 8651-8667, 2013.

548 Liu, D., Li, J., Zhang, Y., Xu, Y., Liu, X., Ding, P., Shen, C., Chen, Y., Tian, C., and Zhang,

549 G.: The use of levoglucosan and radiocarbon for source apportionment of PM$_{2.5}$ carbonaceous

550 aerosols at a background site in East China, Environ. Sci. Technol., 47, 10454-10461, 2013.

551 Muller, C., Iinuma, Y., Boge, O., and Herrmann, H.: Applications of CE-ESI-MS/MS

552 analysis to structural elucidation of methylenecyclohexane ozonolysis products in the particle

553 phase, Electrophoresis, 28, 1364-1370, 2007.

554 Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K.,

555 Segers, A., and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D

556 modeling study, Atmos. Chem. Phys., 11, 5761-5782, 2011.

557 Narukawa, M., Kawamura, K., Takeuchi, N., and Nakajima, T.: Distribution of dicarboxylic

558 acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires,

559 Geophys. Res. Lett., 26, 3101-3104, 1999.

560 Noziere, B., Kalberer, M., Claeys, M., Allan, J., D'Anna, B., Decesari, S., Finessi, E., Glasius,

561 M., Grgic, I., Hamilton, J. F., Hoffmann, T., Iinuma, Y., Jaoui, M., Kahnt, A., Kampf, C. J.,

562 Kourtchev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-Kreis, J., Surratt, J. D.,

563 Szidat, S., Szmigielski, R., and Wisthaler, A.: The molecular identification of organic

564 compounds in the atmosphere: state of the art and challenges, Chem Rev, 115, 3919-3983,

565 2015.

566 Pavuluri, C. M., Kawamura, K., Mihalopoulos, N., and Swaminathan, T.: Laboratory

567 photochemical processing of aqueous aerosols: formation and degradation of dicarboxylic

568 acids, oxocarboxylic acids and α-dicarbonyls, Atmos. Chem. Phys., 15, 7999-8012, 2015.

569 Prabhakar, G., Ervens, B., Wang, Z., Maudlin, L., Coggon, M., Jonsson, H., Seinfeld, J., and

570 Sorooshian, A.: Sources of nitrate in stratocumulus cloud water: Airborne measurements

571 during the 2011 E-PEACE and 2013 NiCE studies, Atmos. Environ., 97, 166-173, 2014.

572 Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simonelt, B. R. T.:

573 Sources of Fine Organic Aerosol .1. Charbroilers and Meat Cooking Operations, Environ.

574 Sci. Technol., 25, 1112-1125, 1991.

575 Sempere, R., and Kawamura, K.: Low molecular weight dicarboxylic acids and related polar

576 compounds in the remote marine rain samples collected from western Pacific, Atmos.

577 Environ., 30, 1609-1619, 1996.

578 Shen, L., and Wang, Y.: Changes in tropospheric ozone levels over the Three Representative

579 Regions of China observed from space by the Tropospheric Emission Spectrometer (TES),

580 2005–2010, Chin. Sci. Bull., 57, 2865-2871, 2012.

581 Sorooshian, A., Varutbangkul, V., Brechtel, F. J., Ervens, B., Feingold, G., Bahreini, R.,

582 Murphy, S. M., Holloway, J. S., Atlas, E. L., Buzorius, G., Jonsson, H., Flagan, R. C., and

583 Seinfeld, J. H.: Oxalic acid in clear and cloudy atmospheres: Analysis of data from

584   International Consortium for Atmospheric Research on Transport and Transformation 2004,

585   J. Geophys. Res., 111, D23s45, 2006.

586   Sorooshian, A., Lu, M.-L., Brechtel, F. J., Jonsson, H., Feingold, G., Flagan, R. C., and

587   Seinfeld, J. H.: On the source of organic acid aerosol layers above clouds, Environ. Sci.

588   Technol., 41, 4647-4654, 2007a.

589   Sorooshian, A., Ng, N. L., Chan, A. W., Feingold, G., Flagan, R. C., and Seinfeld, J. H.:

590   Particulate organic acids and overall water‐soluble aerosol composition measurements from

591   the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), Journal

592   of Geophysical Research: Atmospheres (1984–2012), 112, 2007b.

593   Sorooshian, A., Csavina, J., Shingler, T., Dey, S., Brechtel, F. J., Sáez, A. E., and Betterton,

594   E. A.: Hygroscopic and chemical properties of aerosols collected near a copper smelter:

595   implications for public and environmental health, Environ. Sci. Technol., 46, 9473-9480,

596   2012.

597   Sorooshian, A., Wang, Z., Coggon, M. M., Jonsson, H. H., and Ervens, B.: Observations of

598   Sharp Oxalate Reductions in Stratocumulus Clouds at Variable Altitudes: Organic Acid and

599   Metal Measurements During the 2011 E-PEACE Campaign, Environ. Sci. Technol., 47,

600   7747-7756, 2013.

601   Sorooshian, A., Crosbie, E., Maudlin, L. C., Youn, J. S., Wang, Z., Shingler, T., Ortega, A.

602   M., Hersey, S., and Woods, R. K.: Surface and airborne measurements of organosulfur and

603   methanesulfonate over the western United States and coastal areas, J. Geophys. Res., 120,

604   8535-8548, 2015.

605   Su, M., Lin, Y., Fan, X., Peng, L., and Zhao, C.: Impacts of global emissions of CO, NO x,

606   and CH 4 on China tropospheric hydroxyl free radicals, Adv. Atmos. Sci., 29, 838-854, 2012.

607   Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A.,

608   Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.:

609   Chemical composition of secondary organic aerosol formed from the photooxidation of

610   isoprene, J. Phys. Chem. A, 110, 9665-9690, 2006.

611   Talbot, R. W., Vijgen, A. S., and Harriss, R. C.: Soluble Species in the Arctic Summer

612   Troposphere - Acidic Gases, Aerosols, and Precipitation, J. Geophys. Res., 97, 16531-16543,

613   1992.

614   Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Effects of Precursor Concentration

615   and Acidic Sulfate in Aqueous Glyoxal−OH Radical Oxidation and Implications for

616   Secondary Organic Aerosol, Environ. Sci. Technol., 43, 8105-8112, 2009.

617   Wang, G., Niu, S., Liu, C., and Wang, L.: Identification of dicarboxylic acids and aldehydes

618   of PM10 and PM2.5 aerosols in Nanjing, China, Atmos. Environ., 36, 1941-1950, 2002.

619 Wang, G. H., Kawamura, K., Hatakeyama, S., Takami, A., Li, H., and Wang, W.: Aircraft

620 measurement of organic aerosols over China, Environ. Sci. Technol., 41, 3115-3120, 2007.

621 Wang, W., Kourtchev, I., Graham, B., Cafmeyer, J., Maenhaut, W., and Claeys, M.:

622 Characterization of oxygenated derivatives of isoprene related to 2-methyltetrols in

623 Amazonian aerosols using trimethylsilylation and gas chromatography/ion trap mass

624 spectrometry, Rapid Commun. Mass Spectrom., 19, 1343-1351, 2005.

625 Wonaschuetz, A., Sorooshian, A., Ervens, B., Chuang, P. Y., Feingold, G., Murphy, S. M.,

626 Gouw, J., Warneke, C., and Jonsson, H. H.: Aerosol and gas re‐distribution by shallow

627 cumulus clouds: An investigation using airborne measurements, J. Geophys. Res., 117, 2012.

628 Yu, J. Z., Huang, X. F., Xu, J. H., and Hu, M.: When aerosol sulfate goes up, so does oxalate:

629 Implication for the formation mechanisms of oxalate, Environ. Sci. Technol., 39, 128-133,

630 2005.

631 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M.

632 R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K.,

633 DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama,

634 S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S.,

635 Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen,

636 J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated

637 species in organic aerosols in anthropogenically-influenced Northern Hemisphere

638 midlatitudes, Geophys. Res. Lett., 34, L13801, 2007.

639 Zhang, Y.-L., Liu, J.-W., Salazar, G. A., Li, J., Zotter, P., Zhang, G., Shen, R.-r., Schäfer, K.,

640 Schnelle-Kreis, J., Prévôt, A. S. H., and Szidat, S.: Micro-scale (μg) radiocarbon analysis of

641 water-soluble organic carbon in aerosol samples, Atmos. Environ., 97, 1-5, 2014.

642 Zhang, Y.-L., and Cao, F.: Fine particulate matter (PM2.5) in China at a city level, Scientific

643 Reports, 5, 14884, 2015.

644 Zhang, Y. L., Huang, R. J., El Haddad, I., Ho, K. F., Cao, J. J., Han, Y., Zotter, P., Bozzetti,

645 C., Daellenbach, K. R., Canonaco, F., Slowik, J. G., Salazar, G., Schwikowski, M., Schnelle-

646 Kreis, J., Abbaszade, G., Zimmermann, R., Baltensperger, U., Prévôt, A. S. H., and Szidat, S.:

647 Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the

648 extreme winter haze episode of 2013, Atmos. Chem. Phys., 15, 1299-1312, 2015a.

649 Zhang, Y. L., Schnelle-Kreis, J., Abbaszade, G., Zimmermann, R., Zotter, P., Shen, R. R.,

650 Schafer, K., Shao, L., Prevot, A. S., and Szidat, S.: Source Apportionment of Elemental

651 Carbon in Beijing, China: Insights from Radiocarbon and Organic Marker Measurements,

652 Environ. Sci. Technol., 49, 8408-8415, 2015b.

653 Zhang, Y. L., Kawamura, K., Cao, F., and Lee, M.: Stable carbon isotopic compositions of

654 low‐molecular‐weight dicarboxylic acids, oxocarboxylic acids, α‐dicarbonyls, and fatty

655   acids: Implications for atmospheric processing of organic aerosols, J. Geophys. Res., 121,

656   3707-3717, 2016.

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658 **Table 1.** Average concentrations (ng m^{-3}) and concentration ranges (ng m^{-3}) for straight chain
659 diacids (C$_2$–C$_{11}$), branched chain diacids (iC$_4$-iC$_6$), unsaturated diacids (M, F and mM),
660 multifunctional diacids (hC$_4$, kC$_3$ and kC$_7$), oxoacids (ωC$_2$-ωC$_4$, ωC$_9$, and Pyr), and α-
661 dicarbonyls (Gly and MeGly) of aerosol samples collected by aircraft campaigns over China.

	2003 Summer (inland China)		2004 Spring (inland China)		2002/2003 Winter (coastal China)	
	Range	Mean (SD^a)	Range	Mean (SD)	Range	Mean (SD)
Oxalic, C$_2$	36.4-401	183 (111)	76.5-918	286 (216)	13.3-425	92.6 (94.5)
Malonic, C$_3$	6.3-131	54 (35)	12.2-216	57.5 (47.6)	1.4-79	15 (17.9)
Succinic, C$_4$	9.4-277	117 (68.2)	16-319	69.1 (69.9)	2.3-87.9	21.4 (19.8)
Glutaric, C$_5$	20.7-289	159 (79.1)	6.5-73.8	18.1 (16.3)	0.9-26.1	9.7 (7.3)
Adipic, C$_6$	52.3-135	93.9 (23.2)	5.7-69	19.4 (18.1)	3.7-34.5	13.4 (8.1)
Pimelic, C$_7$	0-2.5	0.8 (0.7)	n.d.-8.1	1.7 (2)	0.3-7.5	1.9 (1.7)
Suberic, C$_8$	n.d.^{b}	n.d.	n.d.-2.7	0.2 (0.7)	n.d.-11	3.2 (2.9)
Azelaic,C$_9$	2-13.5	5.6 (3)	2.4-18.2	6.3 (4.3)	2.9-20.6	8.5 (4.8)
Sebacic, C$_{10}$	0.3-3.6	1.3 (1.0)	n.d.-8.4	3.6 (2.5)	0-6.9	1.1 (1.8)
Undecanedioic , C$_{11}$	0.8-4.3	2.1 (0.9)	n.d.-4.3	1.5 (1.3)	n.d.	n.d.
Methylmalonic, iC$_4$	1.2-5.9	3.7 (1.7)	1.1-12.5	4.9 (3)	0-3.9	0.9 (0.9)
Methylsuccinic, iC$_5$	0.6-10.8	4.4 (3.1)	1.3-27.5	5.9 (6.1)	0.7-23.2	5.9 (5.8)
Methylglutaric, iC$_6$	n.d.-1.3	0.4 (0.4)	0.4-5.9	1.2 (1.3)	n.d.-2.8	0.7 (0.8)
Maleic, M	1.8-12.5	6.5 (3.6)	3.3-22.3	9.4 (5)	1.6-11.1	5.7 (2.9)
Fumaric, F	0.1-3.9	1.7 (1.1)	0.5-8.4	3.0 (2.1)	0.1-6.2	1.5 (1.5)
Methylmaleic, mM	2.3-15.1	6.3 (3.6)	2.2-18.0	7.4 (3.8)	1.3-8.2	4 (2)
Hydroxysuccinic, hC$_4$	1.7-12.5	5.3 (3.4)	n.d.-9.3	1.9 (2.2)	n.d.-13.7	1.9 (3.2)
Ketomalonic, kC$_3$	0.4-9.2	4.2 (2.5)	n.d.-22.8	5.6 (5.3)	n.d.-26	5.1 (5.6)
Ketopimelic, kC$_7$	0.4-8.2	3.0 (2.3)	n.d.-18.7	4.0 (4.5)	n.d.-3.9	0.6 (0.9)
Total diacids	139-1230	653 (290)	148-1780	507 (402)	40.4-757	193 (164)
n.s. C$_2$-C$_{11}$	128-1160	615(272)	128-1630	464 (371)	31.3-678	167 (149)
Pyruvic acid, Pyr	n.d.-9.6	2.9 (3.0)	0.1-11.4	2.1 (2.8)	0.7-36.5	10 (8.6)
Glyoxylic, ωC$_2$	8.1-89.6	37.7 (25.2)	8.3-146	46.0 (38.0)	6.7-129	30.6 (28.9)
3-oxopropanoic, ωC$_3$	0.1-9.7	3.3 (2.4)	0.1-1.1	0.5 (0.3)	n.d.-1.9	0.5 (0.5)
4-oxobutanoic, ωC$_4$	0-23.1	8.0 (7.0)	6.8-38.9	14.9 (8.5)	0.6-35.5	7.5 (8.6)
9-oxononoic, ωC$_9$	3.4-36.2	11.6 (8.9)	0.3-20.5	5.8 (5.2)	0.2-5.5	1.8 (1.4)
Total Keto acid	18.7-131	63.5 (36.0)	23.7-178	69.3 (48.5)	12.2-176	50.0 (36.9)
Glyoxal, Gly	0.7-14.8	4.0 (3.6)	0.2-9.5	2.3 (2.5)	0.6-23	4.3 (5.1)
Methylglyoxal, MeGly	0.6-28.2	10.8 (7.7)	0.8-27.3	7.4 (8.3)	2.5-24.3	7.6 (5.6)
Total dicabonyls	1.3-42.9	14.8 (11.1)	1.7-36.8	9.8 (10.7)	3.1-47.3	11.8 (10.5)
Total	170-1390	731 (329)	174-1990	586 (457)	68.5-980	255 (209)
Gly/MeGly	0.1-1.2	0.4 (0.2)	0.04-1.0	0.4 (0.3)	0.2-0.9	0.5 (0.2)
M/F	1.7-13.9	4.9 (2.9)	1.1-13.8	4.5 (3.1)	1.6-27.4	6.8 (6.2)
ωC$_2$/C$_2$	0.1-0.2	0.2 (0.03)	0.1-0.3	0.2 (0.04)	0.2-0.8	0.4 (0.1)
C$_2$/C$_4$	0.6-6.7	2.0 (1.6)	2.9-5.9	4.6 (0.9)	2.8-13.5	4.6 (2.3)
C$_3$/C$_4$	0.2-1.9	0.5 (0.42)	0.7-1.1	0.9 (0.1)	0.4-1.7	0.7 (0.3)
C$_5$/C$_9$	5.2-64.6	31.3 (15.6)	1.6-4.3	2.8 (0.7)	0.1-2.7	1.1 (0.6)
C$_6$/C$_9$	10.0-41.0	19.8 (7.21)	1.3-4.6	2.8 (0.9)	0.5-2.8	1.6 (0.6)

662 ^{a}SD denotes standard deviation (1σ); ^{b}n.d. denotes not detected.

663   **Table 2.** Correlation coefficients (r^2) among oxalic acid (C_2), pyruvic acid (Pyr), glyoxylic acid

664   ($\omega C2$), glyoxal (Gly) and methylglyoxal (MeGly) detected in aerosol samples from aircraft

665   campaigns during summer 2003 (n=14), spring 2004 (n=16) and winter 2002/2003 (n=18) over

666   China. See Table 1 for abbreviations.

Summer 2003					
	C_2	Pyr	ωC_2	Gly	MeGly
C_2	1.00				
Pyr	0.89	1.00			
ωC_2	0.97	0.95	1.00		
Gly	0.75	0.86	0.85	1.00	
MeGly	0.91	0.97	0.97	0.90	1.00

Spring 2004					
	C_2	Pyr	ωC_2	Gly	MeGly
C_2	1.00				
Pyr	0.95	1.00			
ωC_2	0.97	0.93	1.00		
Gly	0.96	0.95	0.97	1.00	
MeGly	0.93	0.92	0.94	0.93	1.00

Winter 2002/2003					
	C_2	Pyr	ωC_2	Gly	MeGly
C_2	1.00				
Pyr	0.70	1.00			
ωC_2	0.98	0.70	1.00		
Gly	0.92	0.69	0.90	1.00	
MeGly	0.85	0.63	0.83	0.94	1.00

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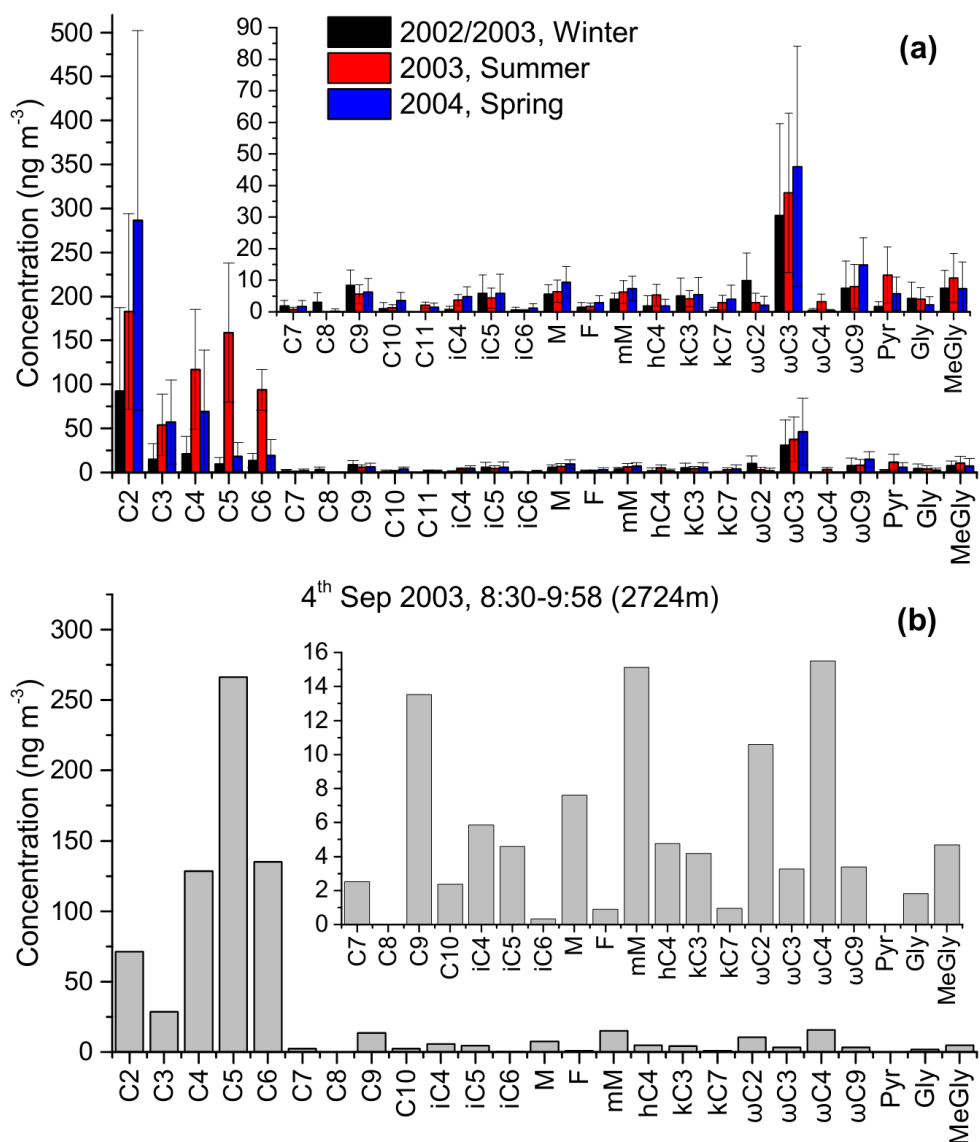
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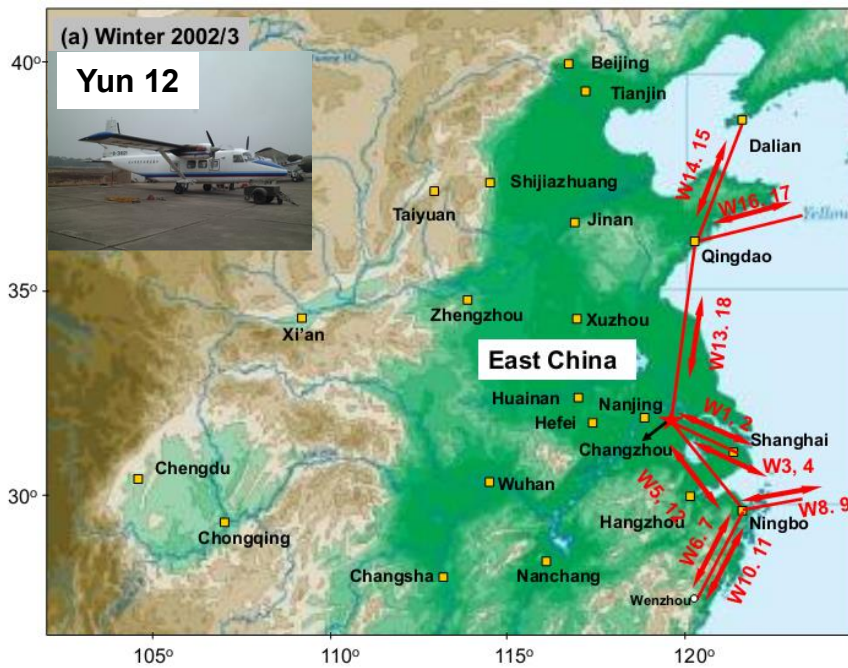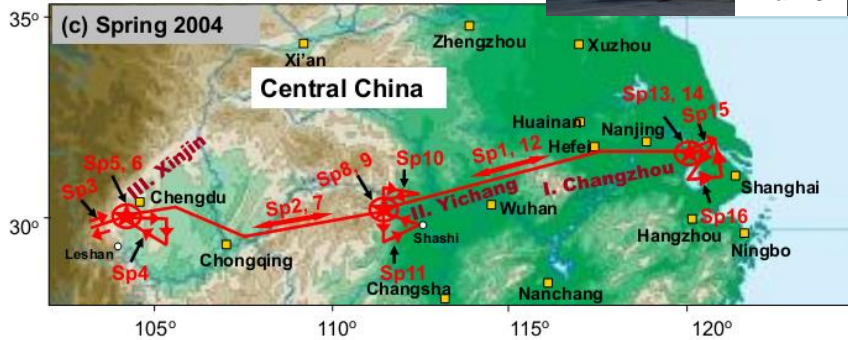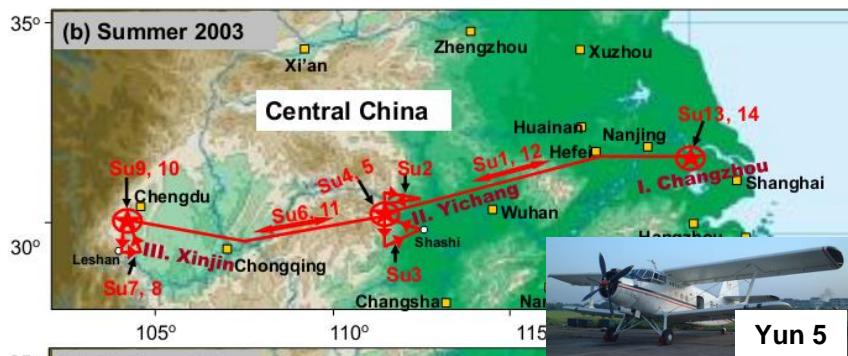

Figure 1. Tracks of research flights during aircraft measurements over China during (a) winter
2002, (b) summer 2003 and (c) spring 2004. The detailed sampling information with flight No.
is listed in the Supplementary Table S1. The maps with the flight tracks were drawn by the
software of PowerPoint 2010, https://products.office.com/.

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Figure 2. Molecular distributions of straight chain diacids (C$_2$–C$_{11}$), branched chain diacids (iC$_4$-iC$_6$), unsaturated diacids (M, F and mM), multifunctional diacids (hC$_4$, kC$_3$ and kC$_7$), ketoacids (ωC$_2$-ωC$_4$, ωC$_9$, and Pyr), and α-dicarbonyls (Gly and MeGly) in aircraft measurement over China; (a) averaged concentrations with bars of standard deviation during winter 2002/2003, summer 2003 and spring 2004; (b) molecular distributions of the measured compounds in the sample collected on 4th Sep 2003. See Table 1 for abbreviations.
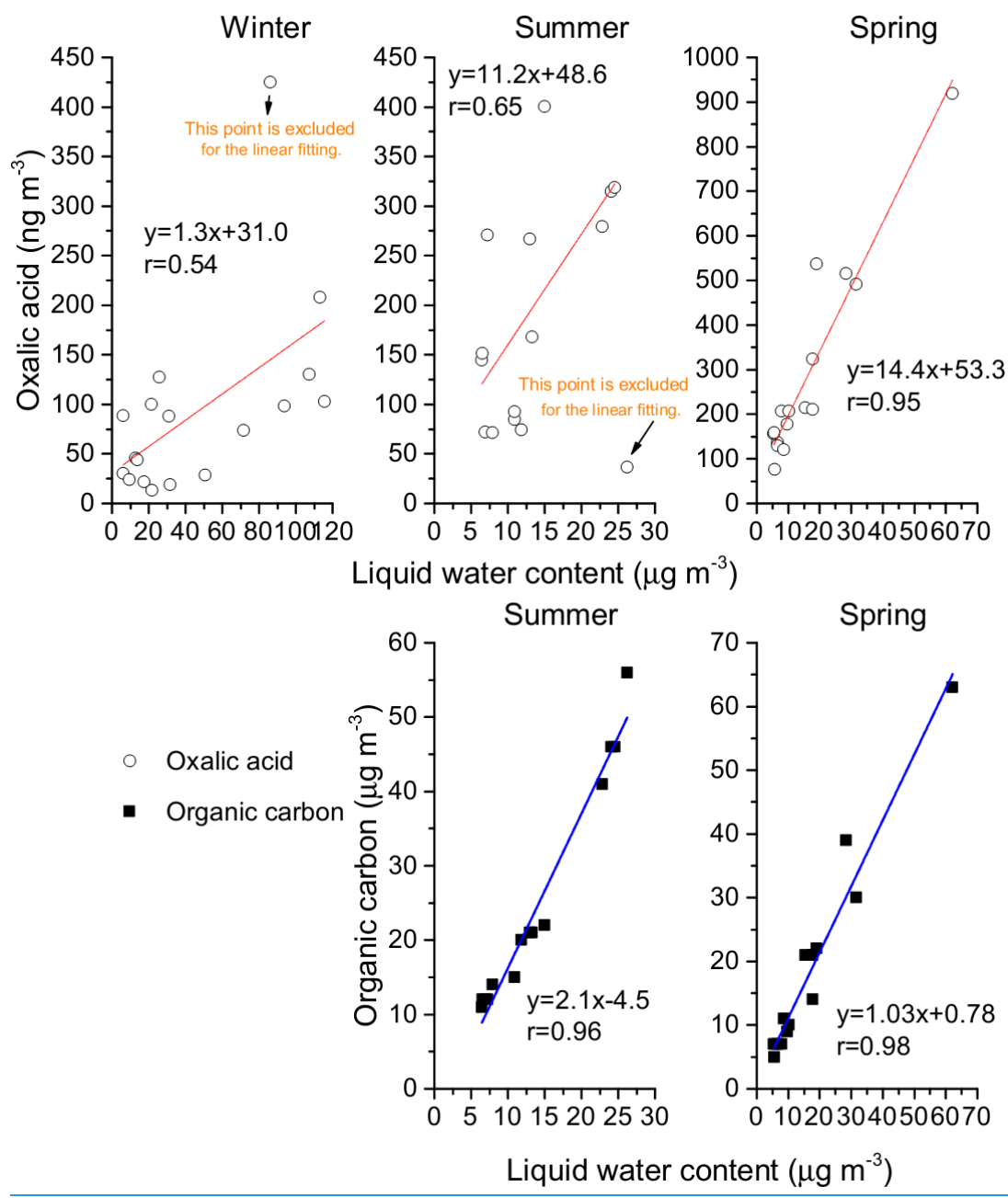
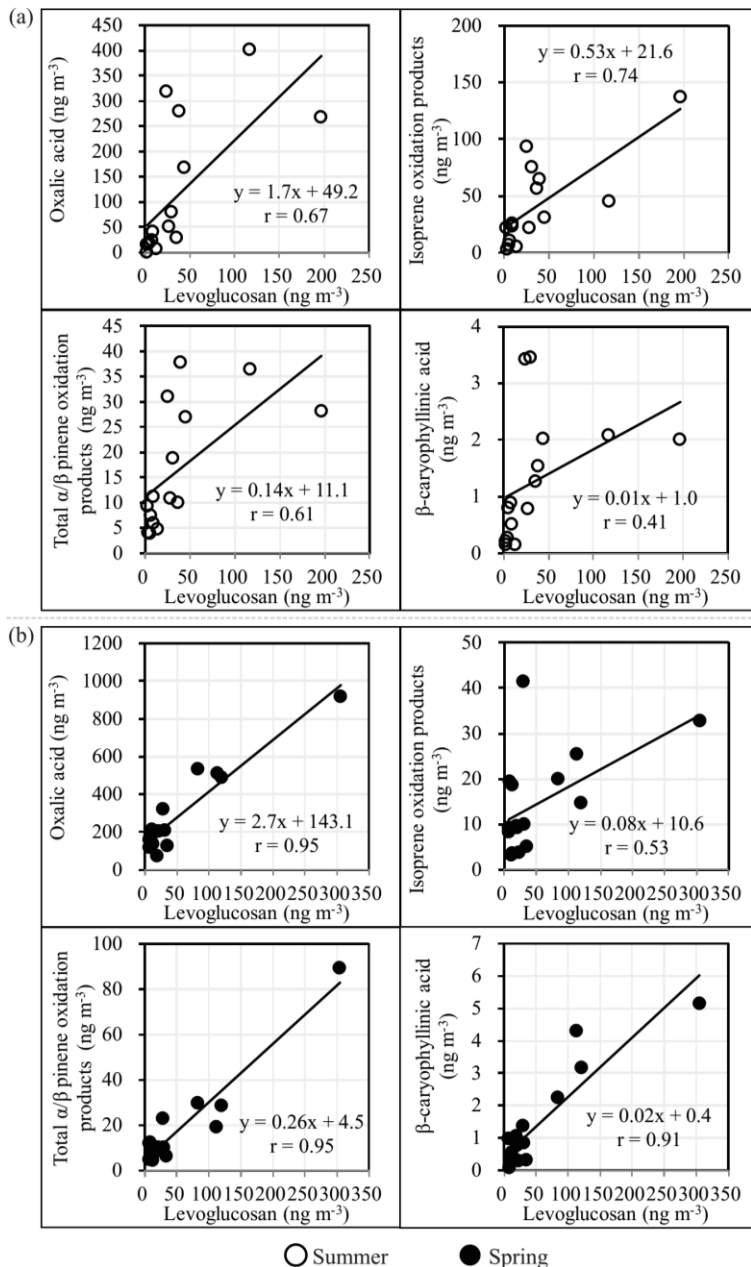**Figure 3**. The linear fitting of the predicted liquid water content with organic carbon (OC) and oxalic acid aerosols during winter, summer, and spring aircraft measurements over China.
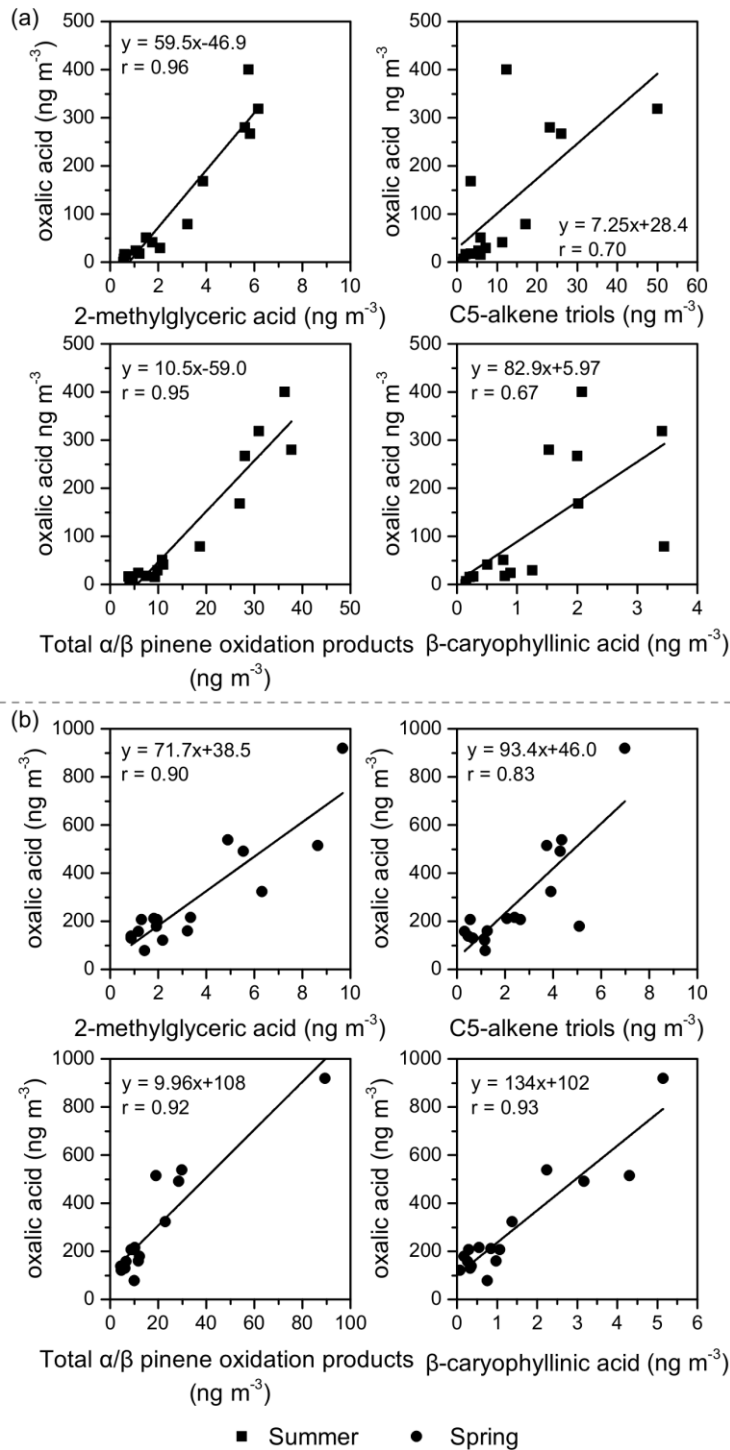
Figure 43. Linear relationship of the concentrations of oxalic acid with the detected tracer compounds for secondary organic aerosols (SOA) such as isoprene SOA tracers such as 2-methylglyceric acid and C5-alkene triols (sub-total of cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene), α/β-pinene SOA tracers (subtotal of 3-hydroxyglutaric acid, pinonic acid, pinic acid, 3-methyl-1,2,3-butanetricarboxylic acid), and β-caryophyllene SOA tracer (i.e., β-caryophyllinic acid) from aircraft measurements over China during (a) summer and (b) spring.

(a)

Oxalic acid (ng m⁻³): y = 1.7x + 49.2, r = 0.67

Isoprene oxidation products (ng m⁻³): y = 0.53x + 21.6, r = 0.74

Total α/β pinene oxidation products (ng m⁻³): y = 0.14x + 11.1, r = 0.61

β-caryophyllinic acid (ng m⁻³): y = 0.01x + 1.0, r = 0.41

(b)

Oxalic acid (ng m⁻³): y = 2.7x + 143.1, r = 0.95

Isoprene oxidation products (ng m⁻³): y = 0.08x + 10.6, r = 0.53

Total α/β pinene oxidation products (ng m⁻³): y = 0.26x + 4.5, r = 0.95

β-caryophyllinic acid (ng m⁻³): y = 0.02x + 0.4, r = 0.91

○ Summer   ● Spring

Figure 5. Linear relationship for the concentrations of levoglucosan with oxalic acid, isoprene SOA tracers, α/β-pinene SOA tracers and β-caryophyllene SOA tracer from the aircraft measurements over China during (a) summer and (b) spring.
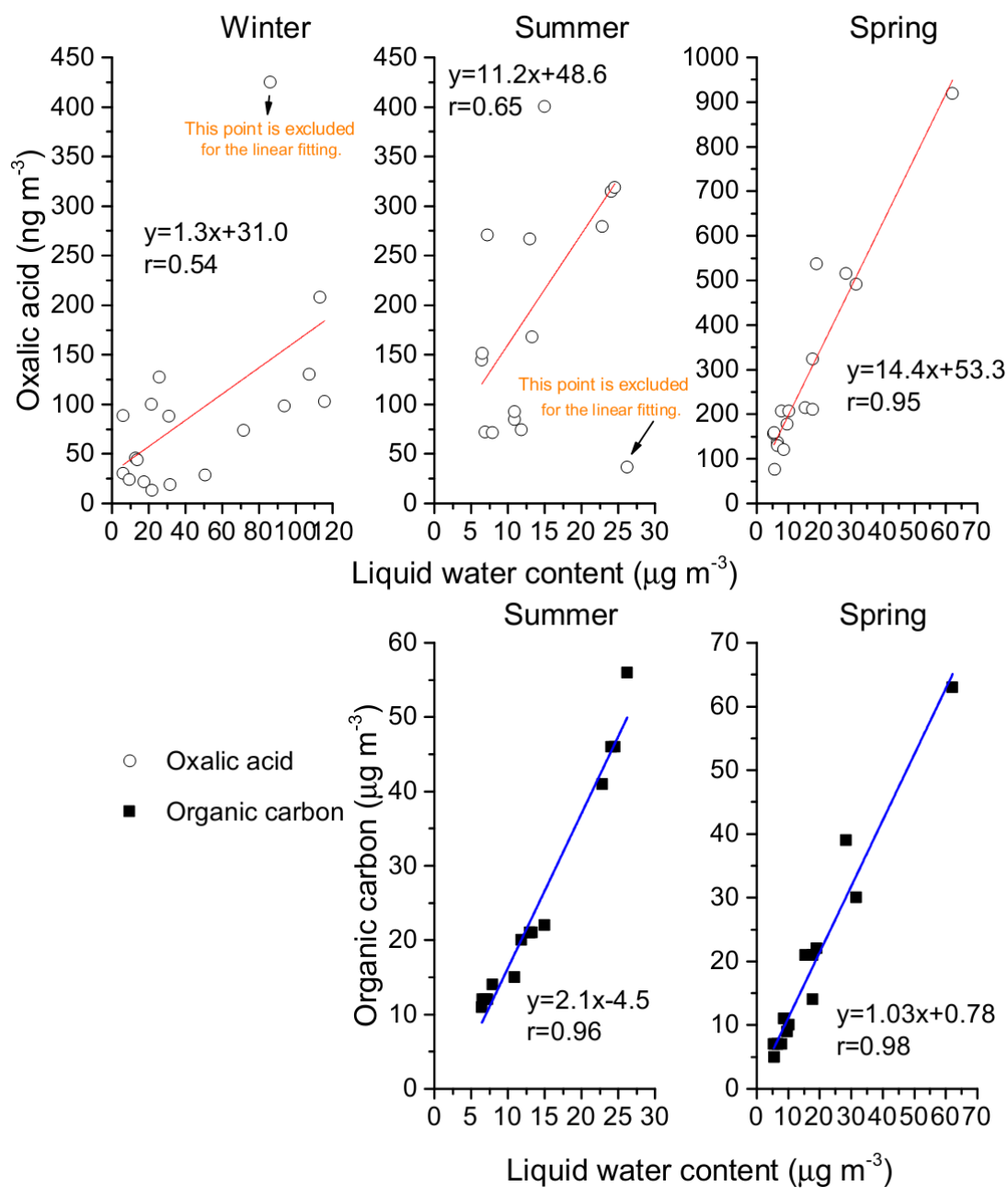
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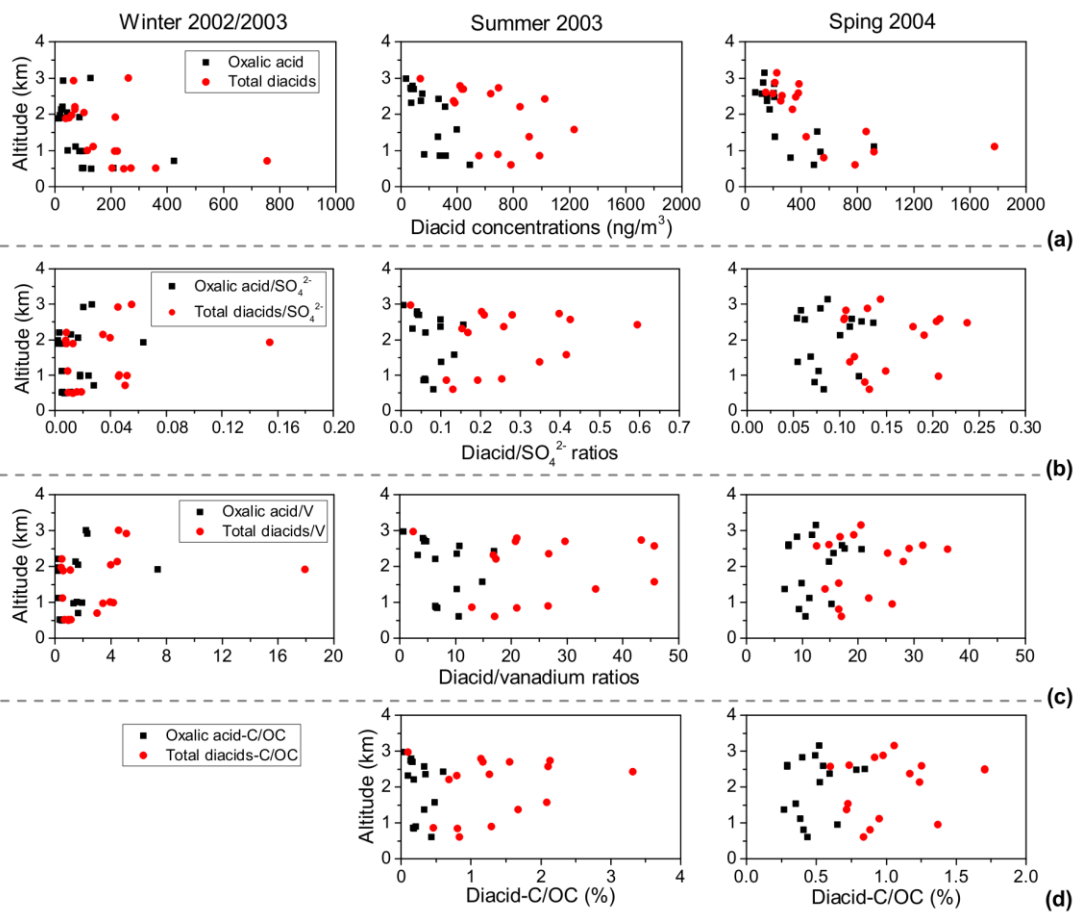
701

702 **Figure 64.** Vertical profiles of (a) concentrations of oxalic acid and total diacids, and their
703 relative abundance to (b) sulfate (SO_4^{2-}), (c) vanadium (V), and (d) organic carbon (OC, %) in
704 aerosol samples collected during winter 2002 (left), summer 2003 (middle) and spring 2004
705 (right) aircraft campaigns over China.

Winter

y=1.3x+31.0
r=0.54

This point is excluded
for the linear fitting.

Summer

y=11.2x+48.6
r=0.65

This point is excluded
for the linear fitting.

Spring

y=14.4x+53.3
r=0.95

Liquid water content (μg m⁻³)

Summer

y=2.1x-4.5
r=0.96

Spring

y=1.03x+0.78
r=0.98

○ Oxalic acid
■ Organic carbon

Liquid water content (μg m⁻³)

706

707 **Figure 5**. The linear fitting of the predicted liquid water content with organic carbon (OC) and
708 oxalic acid aerosols during winter, summer, and spring aircraft measurements over China.