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.

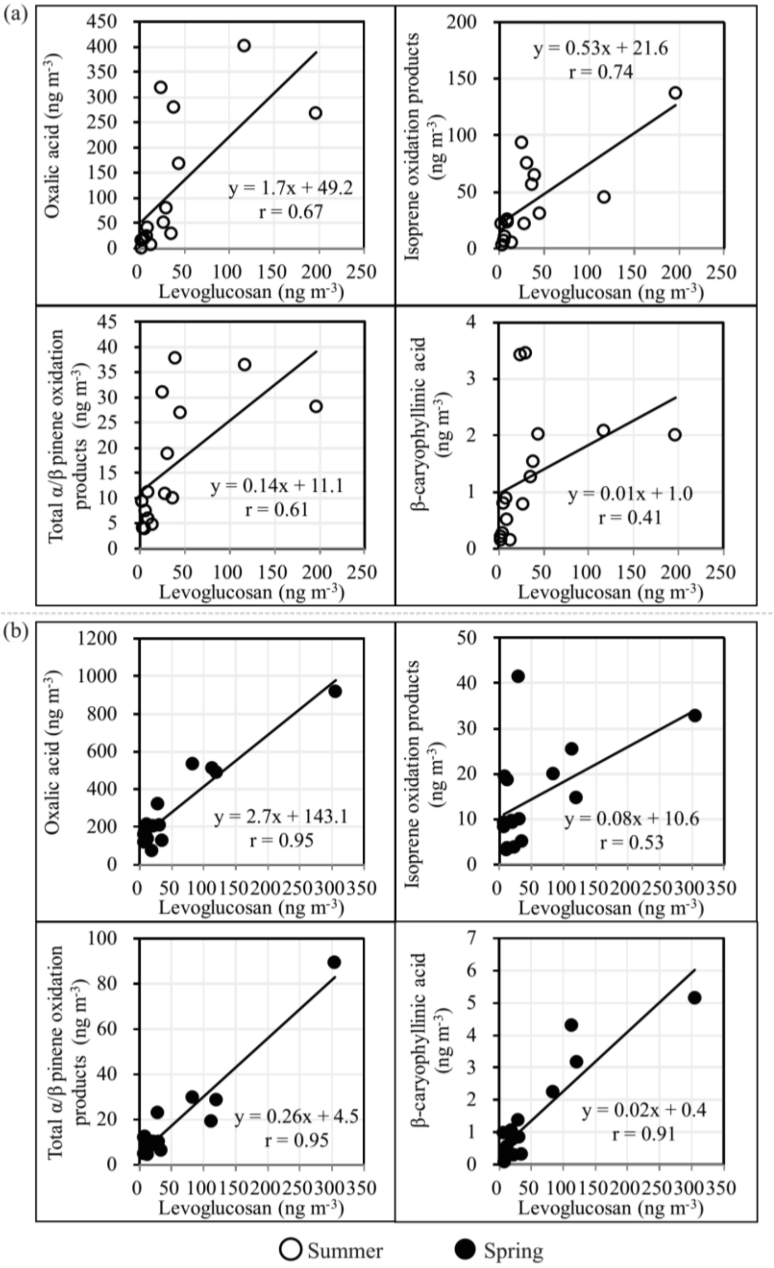

Figure R1. Linear relationship for the concentrations of levoglucosan with oxalic acid, isoprene SOA tracers, α/β-pinene SOA tracers and β-caryophyllene SOA tracer from the aircraft measurements over China during (a) summer and (b) spring.

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

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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 front of Results and Discussion section (Lines277-285). 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 (see lines 194-196 and 255).

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 (lines 218-222).

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.

Aircraft observations of water-soluble dicarboxylic acids in the aerosols over 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 nuclei (CCN) (Kumar et al., 2003). They can contribute to wide ranges from a few percent of the water-soluble mass (Sorooshian et al., 2007b), which could serve as tracers for the atmospheric processing of water-soluble OA (Ervens et al., 2011), to more than 10% of organic carbon (OC) in the remote marine atmosphere (Kawamura and Sakaguchi, 1999).

~~LMW d~~Diacids in aerosols may be directly emitted from fossil fuel combustion (e.g. vehicle exhaust) (Kawamura and Kaplan, 1987), biomass burning (Narukawa et al., 1999) and cooking emissions (Rogge et al., 1991). They can also be formed by degradation from unsaturated fatty acids (Kawamura et al., 1996) and cyclic alkenes (Hatakeyama et al., 1987). Laboratory studies have provided direct experimental evidence that stepwise aqueous oxidation of relatively longer-chain (n) dicarboxylic acids can yield the corresponding short-chain (n-1) dicarboxylic acids (Enami et al., 2015). In addition, in-cloud and below-cloud measurements as well as other field measurements have revealed that aqueous-phase oxidation of volatile organic compounds (VOCs) and intermediates such as glyoxal (Gly), methylglyoxal (MeGly) and pyruvic acid (Pyr) in wet aerosols or clouds and the subsequent gas-particle partitioning are~~is~~ more important pathway for the production of small diacids such as oxalic and malonic acids (Lim et al., 2013;Carlton et al., 2007;Lim et al., 2005;Carlton et al., 2006;Yu et al., 2005;Sorooshian et al., 2007b;Sorooshian et al., 2006;Zhang et al., 2016). Oxalic acid (C_2) is the most abundant diacid with concentrations ranging from a few ng m^{-3} in remote locations (Kawamura et al., 1996) to hundreds or even up to one thousand ng m^{-3} in urban regions (Ho et al., 2007) and highly forested regions (Falkovich et al., 2005). 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). ~~Indeed, it has been reported that photochemical oxidation of isoprene is a predominant formation pathway of oxalic acid (Myriokefalitakis et al., 2011).~~

Most of the previous studies of diacids and other organic compounds in aerosols have been conducted at ground surface; however, only a few aircraft observations that have been conducted over the arctic region (Talbot et al., 1992), the western North Pacific (Narukawa et al., 1999), the western rim of the Pacific Ocean (Kawamura et al., 2003), the coastal marine stratocumulus and cumulus clouds over USA (Crahan et al., 2004;Sorooshian et al., 2013;Sorooshian et al., 2007a;Wonaschuetz et al., 2012;Prabhakar et al., 2014) and over inland agricultural and urban areas in the western United States (Sorooshian et al., 2015). These aircraft experiments have revealed that water-soluble diacids may be produced by the photochemical oxidation of anthropogenic organic compounds in the atmosphere and thus play an important role in controlling the chemical and physical properties of OA in the troposphere. However, the evidence of secondary production of LWM diacids (i.e., oxalic acid) in tropospheric aerosols may be not enough due to the lack of dataset from simultaneous measurements of their possible precursors and/or intermediates such as particle-phase glyoxal (Gly), methylglyoxal (MeGly), pyruvic acid (Pyr) and glyoxylic acid (ωC_2) as well as other secondary organic aerosol (SOA) compounds from photochemical oxidation of VOCs such as isoprene and monoterpenes in the aerosols collected from aircraft campaigns.

East Asia is one of the most important source regions of OA (Zhang et al., 2007), and this is especially true for China due to the rapid urbanization, industrialization and energy consumption (Huang et al., 2014;Zhang et al., 2015a;Zhang and Cao, 2015). Elevated OA were found in the free troposphere ~~(FT)~~ from ACE-Asia aircraft observations, exceeding model-predicted organic aerosols by a factor of 10-100 (Heald et al., 2011;Heald et al., 2005;Henze and Seinfeld, 2006). There is growing evidence that SOA formation from aqueous phase processing of VOCs, especially from isoprene may partially explain the missing OA in the troposphere over East Asia (Heald et al., 2011;Heald et al., 2005;Henze and Seinfeld, 2006), however, vertical profiles of LWM diacids, related organic compounds (i.e., ketoacids and α-dicarbonyls) and SOA tracer compounds in particle phase have not yet been simultaneously analyzed in this region. Additional chemical constraints (e.g. simultaneously measuring different types of organic aerosols such as diacids, ketoacids and α-dicarbonyls and SOA tracer compounds) are urgently required to investigate the importance of SOA formation pathway to the global/regional budget of OA. Our previous studies have reported the molecular composition of primary organic aerosols (POA) including n-alkanes, fatty acids, sugars, and polycyclic aromatic hydrocarbons (PAHs) as well as biogenic SOA tracers in aerosol particles over China (Wang et al., 2007;Fu et al., 2014). However, chemical composition and molecular distribution of ~~LMW~~ diacids have never been reported by aircraft measurements over mainland and coastal China, although only limited studies have been conducted on their spatial distributions based ground observations (Ho et al., 2007).

In this study, we have collected aerosol samples over coastal to inland China using aircraft during spring, summer and winter. The samples were analyzed for a series of LWM diacids and related compounds as well as SOA tracer compounds to investigate the vertical profiles, possible sources and formation pathways of LWM diacids and related organic compounds in the polluted troposphere over China. In light of these analyses, we ~~identified~~ observed that production of oxalic acid and related compounds from anthropogenic and biogenic precursors is enhanced at high altitudes in the troposphere.

2 Materials and Methods

2.1 Aircraft Campaigns

Aircraft measurements were carried out over the coastal East China Sea in winter (12/25/2002−01/06/2003, n=18) and inland China during summer (08/08/2003−09/13/2003, n=14) and spring (05/19/2004−06/10/2004, n=16) using Yun-12 and Yun-5 airplanes as described elsewhere(Wang et al., 2007;Fu et al., 2014) . The sampling heights were from 500 m to 3000 m (with uncertainty of around 10%) above ground level across many major cities such as Changzhou, Nanjing, Hefei, Wuhan, Chongqing and Chengdu for inland aerosol samples as well as Wenzhou, Ningbo, Shanghai, Changzhou, Qingdao and Dalian for coastal aerosol samples. The detailed flight tracks and flight information are shown in Figure 1 and Table S1 (see Supporting Information). $PM_{2.5}$ aerosols were collected on pre-heated quartz fiber filter (diameter of 90 mm) using a medium-volume air sampler (Beijing Geological

Instrument Factory, China). Aerosol samples were collected for the sampling period from ca. 80 min. to two hours. Air was taken via an inlet installed below the cabin of the aircraft at a flow rate of 78 L/min. 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.

2.2 Measurement of ~~LMW~~ diacids

~~LMW d~~Diacids and related organic compounds such as ω-oxocarboxylic acids (or oxoacids), pyruvic acid and α-dicarbonyls were determined as described elsewhere (Kawamura and Ikushima, 1993;Ho et al., 2010). Briefly, the sample and blank filters were extracted with organic free ultrapure water (10 ml × 3) in a glass vial for 10 min. To remove insoluble particles and filter debris, the extracts were passed through a Pasteur pipette packed with quartz wool. The combined extracts were concentrated using a rotary evaporator under a vacuum and then further concentrated using a nitrogen blow-down system. The concentrated extracts were reacted with 14% BF_3/n-butanol to derive carboxyl group to dibutyl ester and oxo group to dibutoxy acetals.

The derivatives were extracted with n-hexane, concentrated to near dryness, dissolved with n-hexane in 1.5 ml glass vials. The samples were finally determined using a gas chromatography (GC, HP6980) with a split/splitless injection, fused silica capillary column (HP-5, 0.2 mm i.d. x 25 m long x 0.52 µm film thickness) and a flame ionization detector. Identification of the compounds was performed by GC retention times with those of authentic standards and GC/mass spectrometry analyses. Recoveries of authentic standards spiked to a pre-heated quartz fiber filter were generally better than 85% for all organic compound identified except for oxalic acid (78%), pyruvic acid (72%), and methylglyoxal (55%). Duplicate analyses of filter samples from other sites indicated that analytical errors are smaller than 15%. During the aircraft campaigns, field blank filters were mounted onto the sampler for seconds without pumping. Blank and sample filters were placed individually in a clean (pre-combusted at 450 °C for 6 h) glass jar sealed with a Teflon-lined screw cap, transported to the laboratory, and stored at -20 °C prior to analysis (Wang et al., 2007).

Small peaks of oxalic, malonic and glyoxylic acids were found in the field and lab blanks, but they were smaller than 10% of the real samples. The concentrations reported here are all corrected for the field blanks but not for the recoveries. The method of SOA tracers measurement was described elsewhere (Fu et al., 2014) .

2.3 Measurements of EC and OC

The concentrations of organic carbon (OC) and elemental carbon (EC) were measured with thermal-optical transmittance method by OC/EC Carbon Aerosol Analyzer (Sunset Laboratory Inc., USA) following the IMPROVE protocol (Chow et al., 2004). All the analyses of the filter samples were completed in 2006.

2.4 Estimation of liquid water content and aerosol acidity

Liquid water content (LWC) and aerosol acidity were predicted by ISORROPIA II, which is a thermodynamic equilibrium model with robust and rapid convergence for all aerosol types (Fountoukis and Nenes, 2007). Measured concentrations of water-soluble inorganic ions, ambient temperature and relative humility were used as input.

3 Results and discussion

3.1 Concentrations and molecular distributions

Total concentrations of LWM diacids and related compounds quantified in the inland aircraft $PM_{2.5}$ (i.e., particulate matter with a diameter smaller than 2.5 μm) are 730±328 and 586±457 ng m^{-3} during summer and spring, respectively, while in the coastal aerosols, the average concentration is 254±209 ng m^{-3} in winter (Table 1). It is of great interest to note that the concentrations of diacids in the troposphere~~FT~~ over the Arctic and North Pacific are generally much lower than those reported at ground levels (Kawamura et al., 1996;Kawamura and Sakaguchi, 1999); however, the concentrations in the troposphere over mainland China are within the range of or even higher than those reported at ground levels in major cities (Ho et al., 2007;Kawamura and Ikushima, 1993). Due to the enhanced anthropogenic emissions, concentrations of POA (i.e., n-alkanes, fatty acids, sugars, lignin and resin products, sterols, PAHs, and phthalic acids) are higher in winter than those in summer and spring (Wang et al., 2007). In contrast, the concentrations of diacids in summer and spring are 2-15 times higher than those in winter, indicating that these compounds are mostly of secondary origin via the oxidation of their gaseous precursors such as isoprene and α/β-pinene (Kanakidou et al., 2005;Carlton et al., 2006;Carlton et al., 2007;Carlton et al., 2009;Ervens et al., 2011) as discussed below.

Molecular distributions of diacids (C_n is n-numbered carbon diacid) in our study are generally characterized by the predominance of oxalic acid (C_2) followed by succinic (C_4) and malonic (C_3) acids during spring and winter, being consistent with previous findings obtained in Chinese megacities (Ho et al., 2007) (Figure 2a). However, in many summer samples collected at height of above 2 km, we found the predominance of glutaric (C_5) and adipic (C_6) acids (see Figure 2b), which are the major organic compounds produced by the oxidation of anthropogenic cyclohexene and methylenecyclohexane (Hamilton et al., 2006;Muller et al., 2007). Although C5 and C6 diacids are the ozonolysis products in smog chamber studies, Pavuluri et al. (2015) recently proposed that C5 and C6 acids are produced by photochemical processing of aqueous aerosols from a laboratory study. ~~.~~Such a molecular distribution has not been reported for the ~~free~~ tropospheric and ground level aerosols (Hatakeyama et al., 1987;Enami et al., 2015;Kawamura and Bikkina, 2016). In our measurements, the averaged 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 4-20 times higher than those in ground measurements in many megacities in China (Ho et al., 2007), Tokyo (Kawamura and Yasui, 2005) and Los Angeles (Kawamura and Kaplan, 1987). Such high abundances of C_5 and C_6 observed in summer imply an important formation pathway associated with enhanced photochemical oxidation of anthropogenic precursors in the polluted troposphere over China.

3.2 C_3 (C_2) to C_4 ratio

The malonic to succinic acid (C_3/C_4) ratios can provide information on source, formation pathways and photochemical aging of organic aerosols. C_3/C_4 ratios in aerosols derived from vehicular exhausts (i.e., 0.25–0.44, av. 0.35) (Kawamura and Kaplan, 1987) have lower values than those in ambient aerosols from Tokyo (i.e., 0.56–2.9, av. 1.6) (Kawamura and Ikushima, 1993) and China's megacities (i.e., 0.6–1.1, average 0.74) (Ho et al., 2007). In contrast, the ratios are substantially higher for aged aerosols because C_3 is more produced by photochemical processing of C_4 (Kawamura and Ikushima, 1993). Actually, higher C_3/C_4 ratios are observed for remote marine aerosols from the North Pacific including tropic (range: 1–11, av. 3.9) which are subjected to extensive aging during the long-range atmospheric transport (Kawamura and Sakaguchi, 1999). In this study, C_3/C_4 ratios are 0.5±0.4 in summer, 0.9±0.1 in spring (Table 1), and 0.7±0.2 in winter, apparently smaller than those in aerosols affected by atmospheric aging, but similar to that of urban aerosols in China (i.e., 0.9 in summer and 0.6 in winter) (Ho et al., 2007). 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 increasing OH concentrations and solar radiation.

C_2/C_4 ratios (2.0 in summer, 4.6 in spring and 4.6 in winter) in our study are found to be much smaller than those from ground observations in China during summer (inland cities in 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 could be also resulting from degradation of C_2 and C_3 in high altitudes due to increased solar radiation. However, no strong correlation ($p>0.05$) is found between C_2/C_4 (and C_3/C_4) and sampling altitude although solar radiation is expected to increase with increasing altitudes. These results suggest that the degradation of higher homologous diacids (i.e., C_4) is not an important pathway for the production of tropospheric C_2 and C_3 in China, and primary fossil-fuel emissions and/or secondary production from other precursors are major formation pathways of these small diacids (i.e., C_2, C_3 and C_4).

3.3 Cis/trans ratio

It has been revealed that maleic acid (M, *cis* configuration) is produced by photochemical oxidation of anthropogenic aromatic hydrocarbons such as benzene and toluene, which is predominant over fumaric acid (F, *trans* configuration) (Sempere and Kawamura, 1996). M can be photo-isomerized to its *trans* isomer (*F)* in the atmosphere under solar radiation. M/F ratios (4.9, 4.5 and 6.8 for summer, spring and winter, respectively) are much higher in the present study than those reported in marine region (0.1-1.5) (Fu et al., 2013) and Chinese megacities at ground levels (2.0 and 2.2 for summer and winter, respectively) (Ho et al., 2007). This indicates that only a small fraction of maleic acid is isomerized to fumaric acid by photochemical transformation and thus SOA produced from anthropogenic emissions in the lower/middle troposphere in China is mostly fresh without substantially photochemical processing (Cong et al., 2015).

3.4 C_5 (C_6) to C_9 diacid ratio

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 of relative contribution from anthropogenic and biogenic sources to OA (Kawamura and Yasui, 2005). C_6/C_9 and C_5/C_9 ratios during the summer aircraft campaign are on average 17 and 28, respectively, which are >15 times higher than those reported at the ground surface from major Chinese cities (Ho et al., 2007;Wang et al., 2002). This comparison further supports that anthropogenic sources are an important source of OA in the high altitudes over China. Taken 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~~ small 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 ωC_2~~ 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 4~~3~~) (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

As shown in Figure 6~~4~~, the highest concentrations of oxalic acid and total diacids are observed around at 2 km in altitude during summer with a sharp decrease toward 3 km. However, during spring and winter, their concentrations decrease with increasing altitudes due to the atmospheric dilution during upward transport. Much clear trends are observed in the vertical profiles of oxalic acid normalized by anthropogenic tracers such as sulfate (SO_4^{2-}), vanadium, and bulk OC. Interestingly, similar trends are also found in spring and winter samples, but the trends are weaker, suggesting that a secondary production of oxalic acid is largely enhanced ~~in summer~~during summer ~~at higher altitudes of~~ in the upper~~lower~~ troposphere (~2 km). Similar vertical pattern has been also reported for biogenic SOA-tracers such as 2-MGA, 3-HGA and MBTCA (3-methyl-1,2,3-butanetricarboxylic acid), but not for POA such as biomass burning tracers (e.g., levoglucosan), fungal spore tracers (arabitol and mannitol), sucrose, and trehalose (Fu et al., 2014). These results further demonstrate that oxalic acid is mostly likely produced by secondary process in the troposphere.

Oxalic acid ~~and related organic species identified~~ in the high altitudes could not be simply explained by uplifting transport of pre-existing SOA produced on the ground surface because these SOA compounds relative to anthropogenic tracers such as SO_4^{2-}, vanadium, and OC significantly increased with altitude as stated above. This finding suggests that in-situ SOA production by the oxidation of VOCs lifted from ground surface substantially contributes to the observed levels of oxalic acid and related species. Therefore, SOA formation in cloud or wet aerosol via the oxidation of biogenic and anthropogenic VOCs may increase concentrations of oxalic acid at higher altitudes in the ~~lower FT~~troposphere. There is growing evidence to support of in-cloud formation of oxalic acid and related SOA. Many studies suggest that oxalic acid is mostly produced via aqueous-phase oxidation of water-soluble organics such as glyoxal, methylglyoxal, pyruvic acid and glyoxylic acid, which are oxidation intermediates of various VOCs (Ervens et al., 2004;Carlton et al., 2006;Ervens et al., 2011). ~~Indeed, a good correlation (Figure 5) 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. This formation pathway is also supported by the consistently good correlation among these species identified in our study as discussed previously. Aqueous-phase production of oxalic acid and related compounds may increase the abundances of SOA at the lower FT (around 2 km in this study). 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 FT (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.~~

4 Conclusions

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

The present study demonstrates that secondary formation of oxalic acid in aqueous phase plays an important role in the SOA budget from the near surface to the lower FT (i.e., 2 km) over inland China, whereas dilution of pre-existing particles and VOCs, photochemical decomposition and aerosol processing may decrease the levels of oxalic acid and related compounds at higher altitudes (>2 km). Our findings also highlight that water-soluble ~~LMW~~ diacids and other SOA components may ~~control~~ have important impacts on the chemical compositions, physical properties and budget of OA in the polluted troposphere over China, and thus significantly affect the regional/global climate and intercontinental transport especially over the Pacific Ocean.

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References

Carlton, A. G., Turpin, B. J., Lim, H. J., Altieri, K. E., and Seitzinger, S.: Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, Geophys. Res. Lett., 33, L06822, 2006.

Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H. J., and Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, Atmos. Environ., 41, 7588-7602, 2007.

Carlton, A. G., Wiedinmyer, C., and Kroll, J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmos. Chem. Phys., 9, 4987-5005, 2009.

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.

Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., Moosmüller, H., and Fung, K.: Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols, Environ. Sci. Technol., 38, 4414-4422, 2004.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, Science, 303, 1173-1176, 2004.

Cong, Z. Y., Kawamura, K., Kang, S. C., and Fu, P. Q.: Penetration of biomass-burning emissions from South Asia through the Himalayas: new insights from atmospheric organic acids, Scientific Reports, 5, 9580, 2015.

Crahan, K. K., Hegg, D., Covert, D. S., and Jonsson, H.: An exploration of aqueous oxalic acid production in the coastal marine atmosphere, Atmos. Environ., 38, 3757-3764, 2004.

Enami, S., Hoffmann, M. R., and Colussi, A. J.: Stepwise Oxidation of Aqueous Dicarboxylic Acids by Gas-Phase OH Radicals, J. Phys. Chem. Lett., 6, 527-534, 2015.

Ervens, B., Feingold, G., Frost, G. J., and Kreidenweis, S. M.: A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, J. Geophys. Res., 109, D15205, 2004.

Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, Atmos. Chem. Phys., 11, 11069-11102, 2011.

Falkovich, A. H., Graber, E. R., Schkolnik, G., Rudich, Y., Maenhaut, W., and Artaxo, P.: Low molecular weight organic acids in aerosol particles from Rondonia, Brazil, during the biomass-burning, transition and wet periods, Atmos. Chem. Phys., 5, 781-797, 2005.

Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K+-Ca2+-Mg2+-Nh(4)(+)-Na+-SO42--NO3--Cl--H2O aerosols, Atmos. Chem. Phys., 7, 4639-4659, 2007.

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., Kawamura, K., Usukura, K., and Miura, K.: Dicarboxylic acids, ketocarboxylic acids and glyoxal in the marine aerosols collected during a round-the-world cruise, Mar. Chem., 148, 22-32, 2013.

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.

Fu, T. M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, J. Geophys. Res., 113, D15303, 2008.

Hamilton, J. F., Lewis, A. C., Reynolds, J. C., Carpenter, L. J., and Lubben, A.: Investigating the composition of organic aerosol resulting from cyclohexene ozonolysis: low molecular weight and heterogeneous reaction products, Atmos. Chem. Phys., 6, 4973-4984, 2006.

Hatakeyama, S., Ohno, M., Weng, J. H., Takagi, H., and Akimoto, H.: Mechanism for the Formation of Gaseous and Particulate Products from Ozone-Cycloalkene Reactions in Air, Environ. Sci. Technol., 21, 52-57, 1987.

Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H., and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current models, Geophys. Res. Lett., 32, L18809, 2005.

Heald, C. L., Coe, H., Jimenez, J. L., Weber, R. J., Bahreini, R., Middlebrook, A. M., Russell, L. M., Jolleys, M., Fu, T. M., Allan, J. D., Bower, K. N., Capes, G., Crosier, J., Morgan, W. T., Robinson, N. H., Williams, P. I., Cubison, M. J., DeCarlo, P. F., and Dunlea, E. J.: Exploring the vertical profile of atmospheric organic aerosol: comparing 17 aircraft field campaigns with a global model, Atmos. Chem. Phys., 11, 12673-12696, 2011.

Henze, D. K., and Seinfeld, J. H.: Global secondary organic aerosol from isoprene oxidation, Geophys. Res. Lett., 33, L09812, 2006.

Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J., Chow, J. C., and Watson, J. G.: Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China, J. Geophys. Res., 112, D22S27, 2007.

Ho, K. F., Lee, S. C., Ho, S. S. H., Kawamura, K., Tachibana, E., Cheng, Y., and Zhu, T.: Dicarboxylic acids, ketocarboxylic acids, alpha-dicarbonyls, fatty acids, and benzoic acid in urban aerosols collected during the 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006), J. Geophys. Res., 115, 2010.

Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218-222, 2014.

Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M., and Offenberg, J. H.: Secondary organic aerosol formation from the oxidation of a series of sesquiterpenes: alpha-cedrene, beta-caryophyllene, alpha-humulene and alpha-farnesene with O-3, OH and NO3 radicals, Environ. Chem., 10, 178-193, 2013.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, Atmos. Chem. Phys., 5, 1053-1123, 2005.

Kawamura, K., and Kaplan, I. R.: Motor Exhaust Emissions as a Primary Source for Dicarboxylic-Acids in Los-Angeles Ambient Air, Environ. Sci. Technol., 21, 105-110, 1987.

Kawamura, K., and Ikushima, K.: Seasonal-Changes in the Distribution of Dicarboxylic-Acids in the Urban Atmosphere, Environ. Sci. Technol., 27, 2227-2235, 1993.

Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, Atmos. Environ., 30, 1709-1722, 1996.

Kawamura, K., and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, J. Geophys. Res., 104, 3501-3509, 1999.

Kawamura, K., Umemoto, N., Mochida, M., Bertram, T., Howell, S., and Huebert, B. J.: Water-soluble dicarboxylic acids in the tropospheric aerosols collected over east Asia and western North Pacific by ACE-Asia C-130 aircraft, J. Geophys. Res., 108, 2003.

Kawamura, K., and Yasui, O.: Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, Atmos. Environ., 39, 1945-1960, 2005.

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.

Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Lewis, C. W., Bhave, P. V., and Edney, E. O.: Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location, Atmos. Environ., 41, 8288-8300, 2007.

Kumar, P. P., Broekhuizen, K., and Abbatt, J. P. D.: Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species, Atmos. Chem. Phys., 3, 509-520, 2003.

Lim, H. J., Carlton, A. G., and Turpin, B. J.: Isoprene forms secondary organic aerosol through cloud processing: Model simulations, Environ. Sci. Technol., 39, 4441-4446, 2005.

Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role in secondary organic aerosol (SOA) formation, Atmos. Chem. Phys., 10, 10521-10539, 2010.

Lim, Y. B., Tan, Y., and Turpin, B. J.: Chemical insights, explicit chemistry, and yields of secondary organic aerosol from OH radical oxidation of methylglyoxal and glyoxal in the aqueous phase, Atmos. Chem. Phys., 13, 8651-8667, 2013.

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.

Muller, C., Iinuma, Y., Boge, O., and Herrmann, H.: Applications of CE-ESI-MS/MS analysis to structural elucidation of methylenecyclohexane ozonolysis products in the particle phase, Electrophoresis, 28, 1364-1370, 2007.

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.

Narukawa, M., Kawamura, K., Takeuchi, N., and Nakajima, T.: Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, Geophys. Res. Lett., 26, 3101-3104, 1999.

Noziere, B., Kalberer, M., Claeys, M., Allan, J., D'Anna, B., Decesari, S., Finessi, E., Glasius, M., Grgic, I., Hamilton, J. F., Hoffmann, T., Iinuma, Y., Jaoui, M., Kahnt, A., Kampf, C. J., Kourtchev, I., Maenhaut, W., Marsden, N., Saarikoski, S., Schnelle-Kreis, J., Surratt, J. D., Szidat, S., Szmigielski, R., and Wisthaler, A.: The molecular identification of organic compounds in the atmosphere: state of the art and challenges, Chem Rev, 115, 3919-3983, 2015.

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.

Prabhakar, G., Ervens, B., Wang, Z., Maudlin, L., Coggon, M., Jonsson, H., Seinfeld, J., and Sorooshian, A.: Sources of nitrate in stratocumulus cloud water: Airborne measurements during the 2011 E-PEACE and 2013 NiCE studies, Atmos. Environ., 97, 166-173, 2014.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simonelt, B. R. T.: Sources of Fine Organic Aerosol .1. Charbroilers and Meat Cooking Operations, Environ. Sci. Technol., 25, 1112-1125, 1991.

Sempere, R., and Kawamura, K.: Low molecular weight dicarboxylic acids and related polar compounds in the remote marine rain samples collected from western Pacific, Atmos. Environ., 30, 1609-1619, 1996.

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.

Sorooshian, A., Varutbangkul, V., Brechtel, F. J., Ervens, B., Feingold, G., Bahreini, R., Murphy, S. M., Holloway, J. S., Atlas, E. L., Buzorius, G., Jonsson, H., Flagan, R. C., and Seinfeld, J. H.: Oxalic acid in clear and cloudy atmospheres: Analysis of data from

International Consortium for Atmospheric Research on Transport and Transformation 2004, J. Geophys. Res., 111, D23s45, 2006.

Sorooshian, A., Lu, M.-L., Brechtel, F. J., Jonsson, H., Feingold, G., Flagan, R. C., and Seinfeld, J. H.: On the source of organic acid aerosol layers above clouds, Environ. Sci. Technol., 41, 4647-4654, 2007a.

Sorooshian, A., Ng, N. L., Chan, A. W., Feingold, G., Flagan, R. C., and Seinfeld, J. H.: Particulate organic acids and overall water‐soluble aerosol composition measurements from the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), Journal of Geophysical Research: Atmospheres (1984–2012), 112, 2007b.

Sorooshian, A., Csavina, J., Shingler, T., Dey, S., Brechtel, F. J., Sáez, A. E., and Betterton, E. A.: Hygroscopic and chemical properties of aerosols collected near a copper smelter: implications for public and environmental health, Environ. Sci. Technol., 46, 9473-9480, 2012.

Sorooshian, A., Wang, Z., Coggon, M. M., Jonsson, H. H., and Ervens, B.: Observations of Sharp Oxalate Reductions in Stratocumulus Clouds at Variable Altitudes: Organic Acid and Metal Measurements During the 2011 E-PEACE Campaign, Environ. Sci. Technol., 47, 7747-7756, 2013.

Sorooshian, A., Crosbie, E., Maudlin, L. C., Youn, J. S., Wang, Z., Shingler, T., Ortega, A. M., Hersey, S., and Woods, R. K.: Surface and airborne measurements of organosulfur and methanesulfonate over the western United States and coastal areas, J. Geophys. Res., 120, 8535-8548, 2015.

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.

Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, J. Phys. Chem. A, 110, 9665-9690, 2006.

Talbot, R. W., Vijgen, A. S., and Harriss, R. C.: Soluble Species in the Arctic Summer Troposphere - Acidic Gases, Aerosols, and Precipitation, J. Geophys. Res., 97, 16531-16543, 1992.

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., Niu, S., Liu, C., and Wang, L.: Identification of dicarboxylic acids and aldehydes of PM10 and PM2.5 aerosols in Nanjing, China, Atmos. Environ., 36, 1941-1950, 2002.

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.

Wang, W., Kourtchev, I., Graham, B., Cafmeyer, J., Maenhaut, W., and Claeys, M.: Characterization of oxygenated derivatives of isoprene related to 2-methyltetrols in Amazonian aerosols using trimethylsilylation and gas chromatography/ion trap mass spectrometry, Rapid Commun. Mass Spectrom., 19, 1343-1351, 2005.

Wonaschuetz, A., Sorooshian, A., Ervens, B., Chuang, P. Y., Feingold, G., Murphy, S. M., Gouw, J., Warneke, C., and Jonsson, H. H.: Aerosol and gas re‐distribution by shallow cumulus clouds: An investigation using airborne measurements, J. Geophys. Res., 117, 2012.

Yu, J. Z., Huang, X. F., Xu, J. H., and Hu, M.: When aerosol sulfate goes up, so does oxalate: Implication for the formation mechanisms of oxalate, Environ. Sci. Technol., 39, 128-133, 2005.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophys. Res. Lett., 34, L13801, 2007.

Zhang, Y.-L., Liu, J.-W., Salazar, G. A., Li, J., Zotter, P., Zhang, G., Shen, R.-r., Schäfer, K., Schnelle-Kreis, J., Prévôt, A. S. H., and Szidat, S.: Micro-scale (μg) radiocarbon analysis of water-soluble organic carbon in aerosol samples, Atmos. Environ., 97, 1-5, 2014.

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

Zhang, Y. L., Huang, R. J., El Haddad, I., Ho, K. F., Cao, J. J., Han, Y., Zotter, P., Bozzetti, C., Daellenbach, K. R., Canonaco, F., Slowik, J. G., Salazar, G., Schwikowski, M., Schnelle-Kreis, J., Abbaszade, G., Zimmermann, R., Baltensperger, U., Prévôt, A. S. H., and Szidat, S.: Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode of 2013, Atmos. Chem. Phys., 15, 1299-1312, 2015a.

Zhang, Y. L., Schnelle-Kreis, J., Abbaszade, G., Zimmermann, R., Zotter, P., Shen, R. R., Schafer, K., Shao, L., Prevot, A. S., and Szidat, S.: Source Apportionment of Elemental Carbon in Beijing, China: Insights from Radiocarbon and Organic Marker Measurements, Environ. Sci. Technol., 49, 8408-8415, 2015b.

Zhang, Y. L., Kawamura, K., Cao, F., and Lee, M.: Stable carbon isotopic compositions of low‐molecular‐weight dicarboxylic acids, oxocarboxylic acids, α‐dicarbonyls, and fatty acids: Implications for atmospheric processing of organic aerosols, J. Geophys. Res., 121, 3707-3717, 2016.

Table 1. Average concentrations (ng m^{-3}) and concentration ranges (ng m^{-3}) for 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), oxoacids (ωC_2-ωC_4, ωC_9, and Pyr), and α-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)
$\omega C_2/C_2$	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)

[a]SD denotes standard deviation (1σ); [b]n.d. denotes not detected.

Table 2. Correlation coefficients (r^2) among oxalic acid (C_2), pyruvic acid (Pyr), glyoxylic acid (ωC2), glyoxal (Gly) and methylglyoxal (MeGly) detected in aerosol samples from aircraft campaigns during summer 2003 (n=14), spring 2004 (n=16) and winter 2002/2003 (n=18) over 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

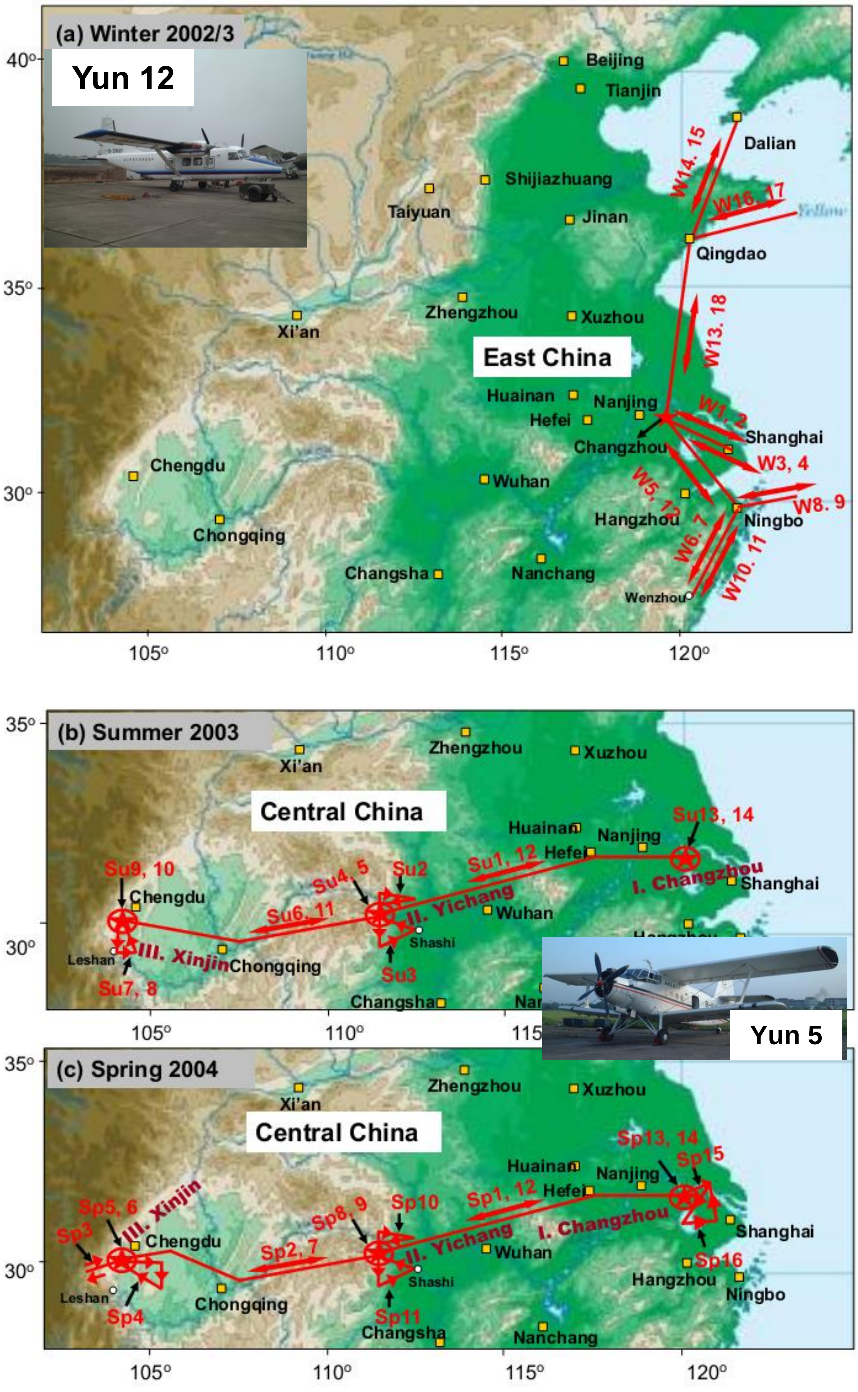


Figure 1. Tracks of research flights during aircraft measurements over China during (a) winter 2002, (b) summer 2003 and (c) spring 2004. The detailed sampling information with flight No. is listed in the Supplementary Table S1. The maps with the flight tracks were drawn by the software of PowerPoint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

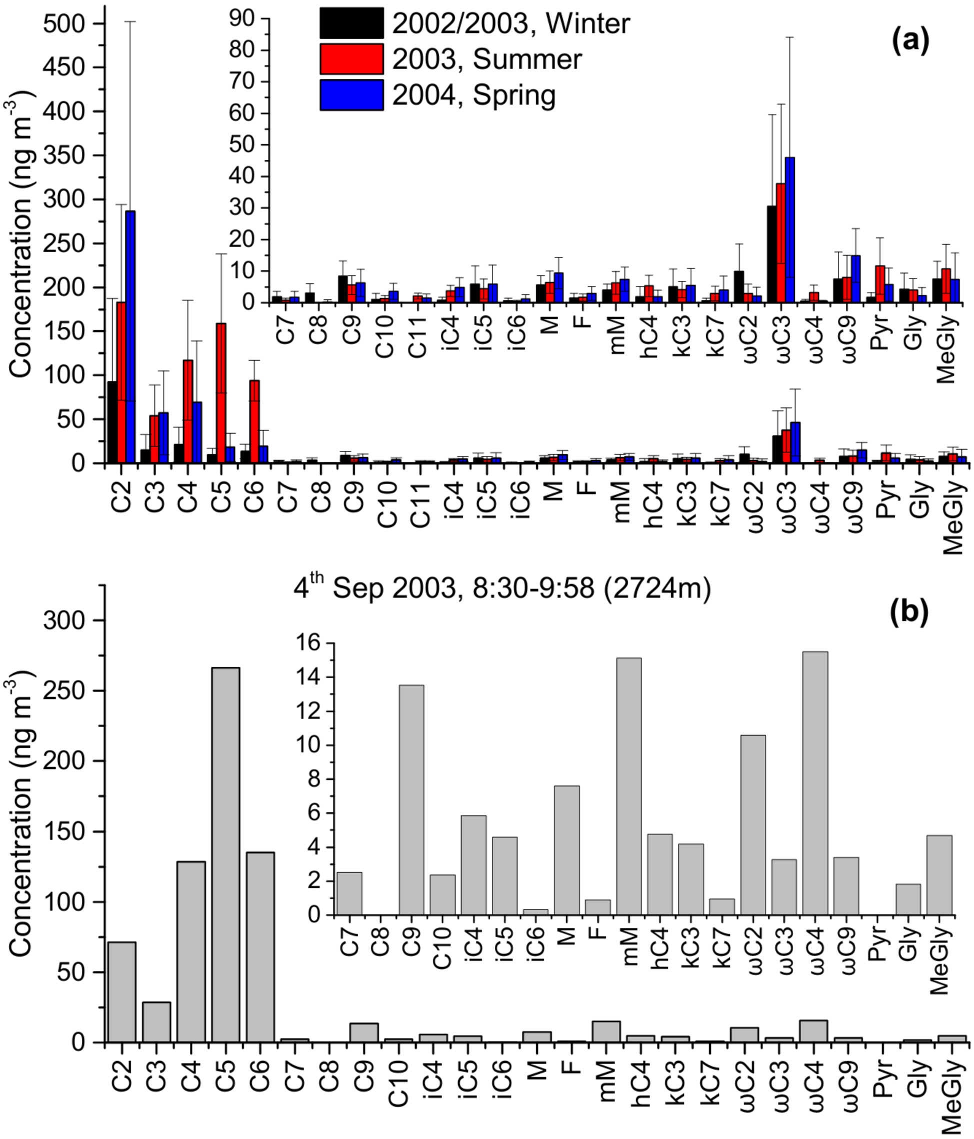


Figure 2. Molecular distributions of straight chain diacids (C_2–C_{11}), branched chain diacids (iC_4-iC_6), unsaturated diacids (M, F and mM), multifunctional diacids (hC_4, kC_3 and kC_7), ketoacids (ωC_2-ωC_4, ωC_9, and Pyr), and α-dicarbonyls (Gly and MeGly) in aircraft measurement over China; (a) 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.

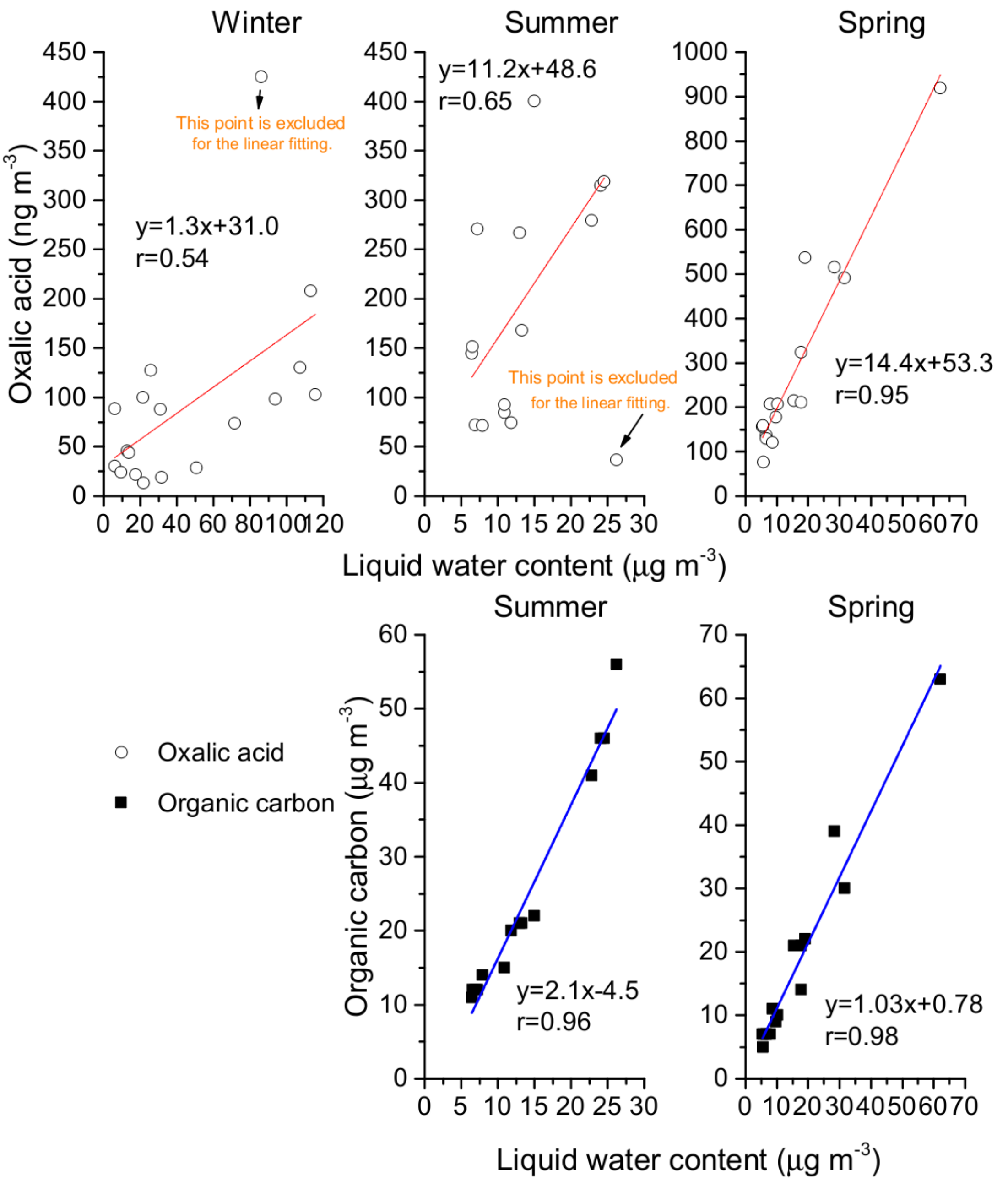


Figure 3. The linear fitting of the predicted liquid water content with organic carbon (OC) and oxalic acid aerosols during winter, summer, and spring aircraft measurements over China.

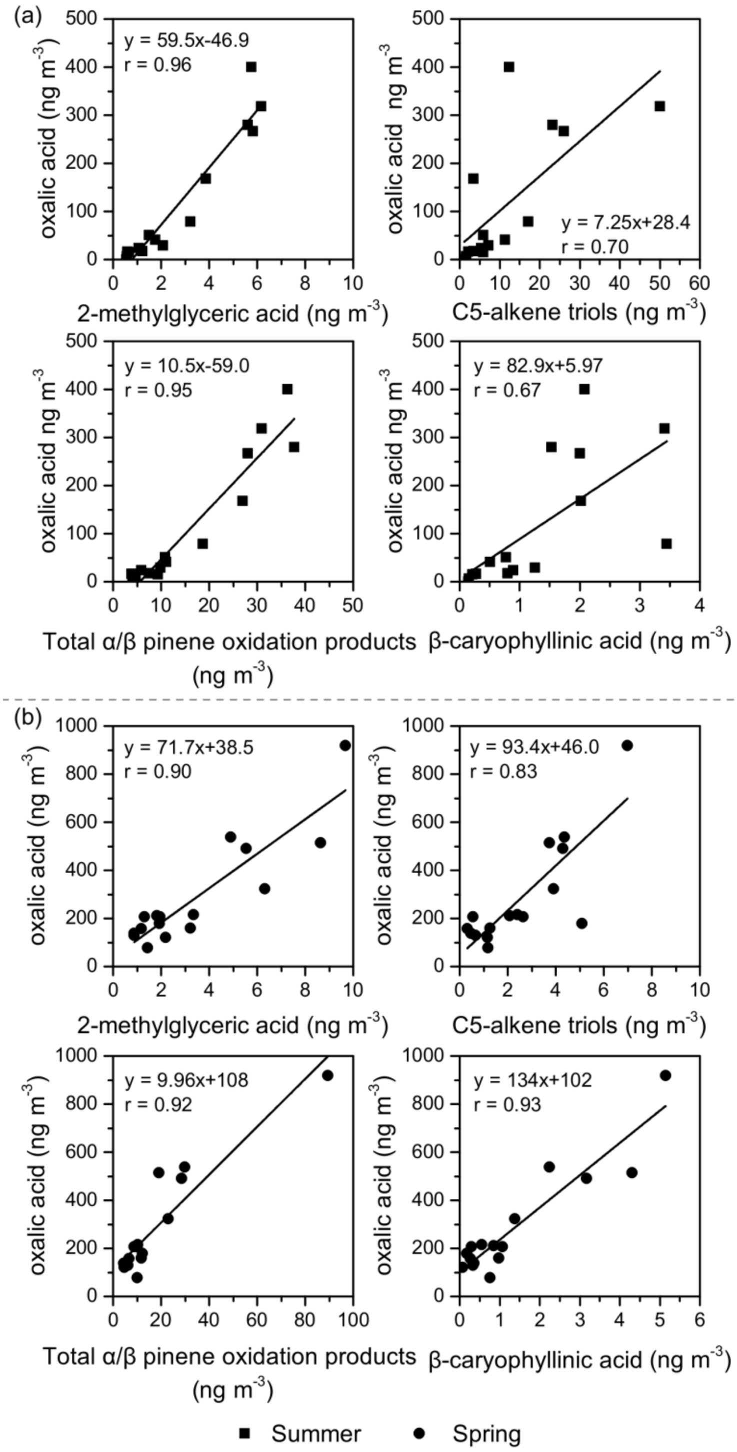


Figure 4~~3~~. Linear relationship of the concentrations of oxalic acid with the detected tracer compounds for secondary organic aerosols (SOA) such as isoprene SOA tracers such as 2-methylglyceric acid and C5-alkene triols (sub-total of cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, 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.

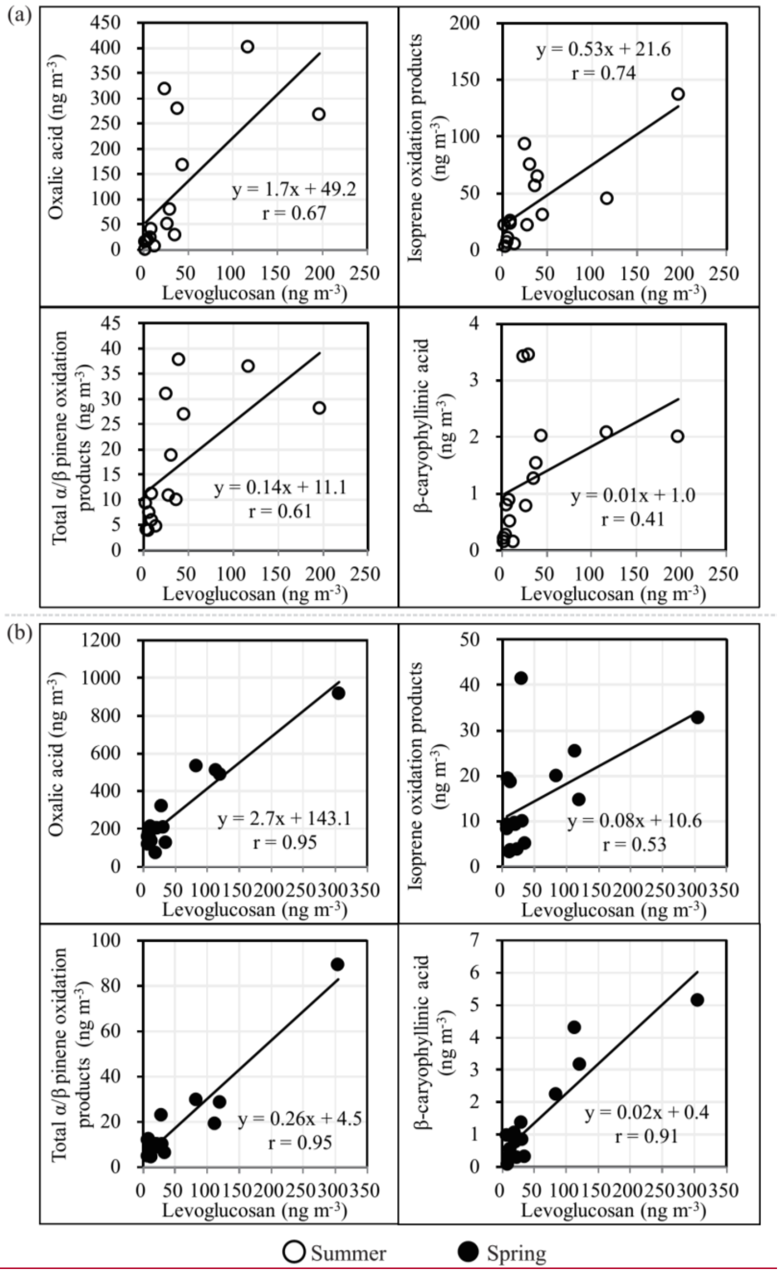


Figure 5. Linear relationship for the concentrations of levoglucosan with oxalic acid, isoprene SOA tracers, α/β-pinene SOA tracers and β-caryophyllene SOA tracer from the aircraft measurements over China during (a) summer and (b) spring.

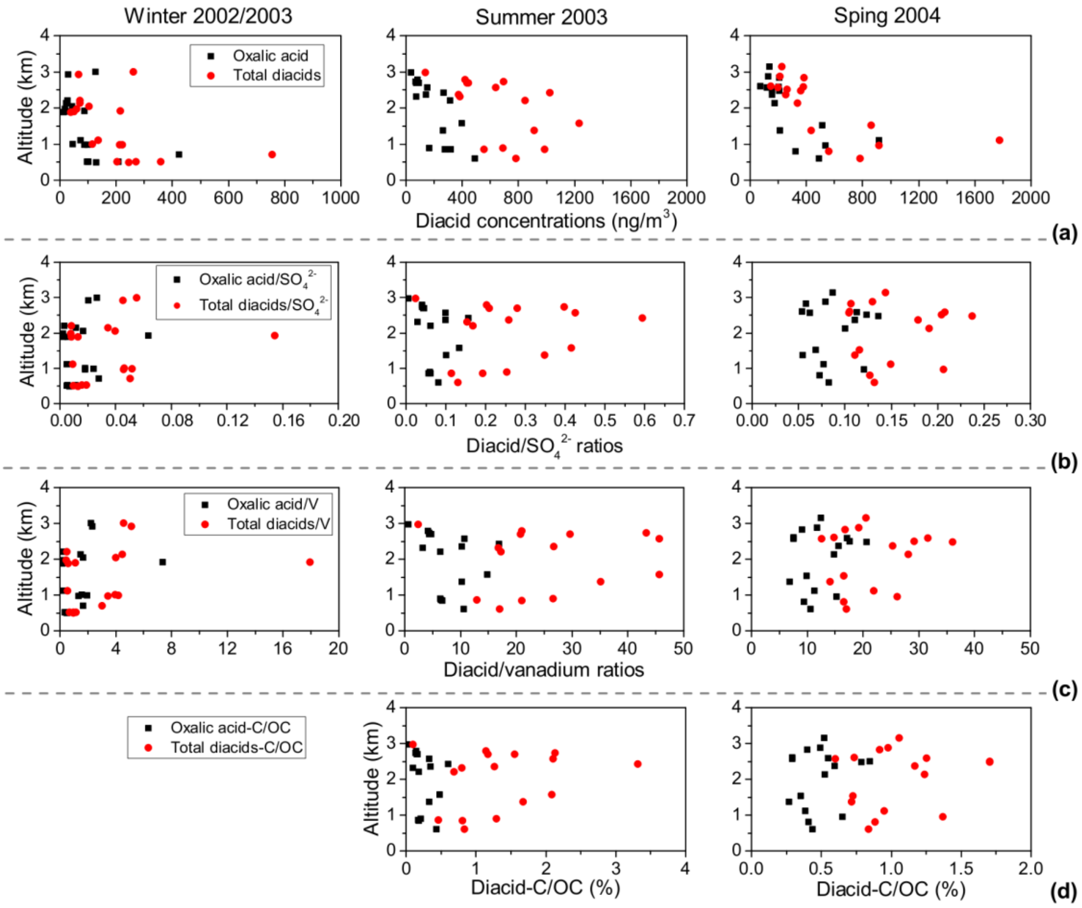
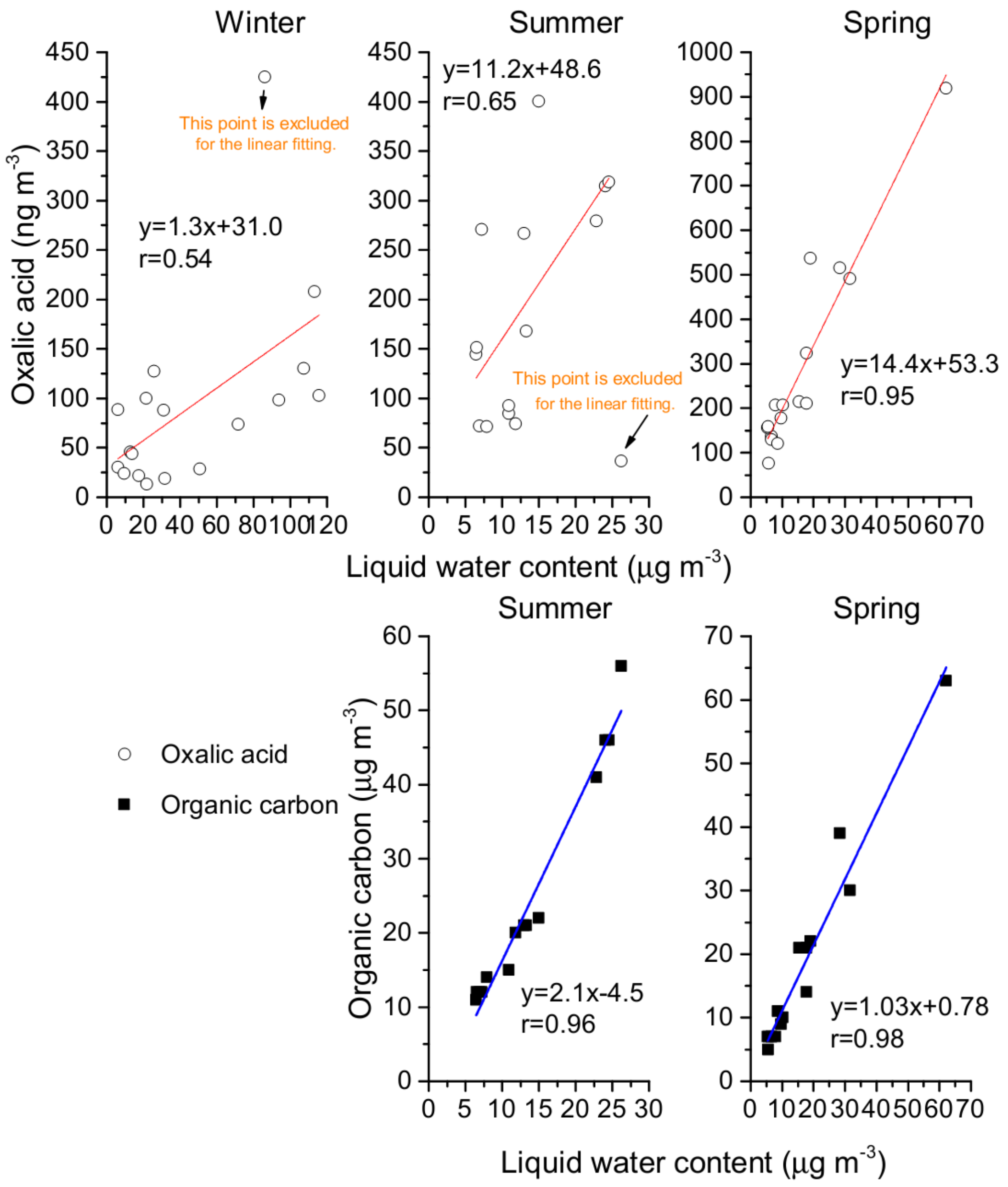


Figure 64. Vertical profiles of (a) concentrations of oxalic acid and total diacids, and their relative abundance to (b) sulfate (SO_4^{2-}), (c) vanadium (V), and (d) organic carbon (OC, %) in aerosol samples collected during winter 2002 (left), summer 2003 (middle) and spring 2004 (right) aircraft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



~~**Figure 5**. 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.~~