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

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Abstract

Vertical profiles of 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 troposphere. Here, we found consistently good correlation of oxalic acid, the most abundant individual organic compounds in aerosols 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

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). As important components of aerosols, diacids play an important role 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).

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 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). 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 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 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 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 diacids

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 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 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 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 andMeGly 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). 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.

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 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 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) (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 over China is of secondary origin, i.e., via aqueous chemistry. This study highlights that oxalic acid may serve as an important tracer of SOA formation not only on the ground surface but also at high altitudes within the lower/middle troposphere. 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.

3.6 Vertical profiles of LWM-diacids

As shown in Figure 6, 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 during summer in the upper 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 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 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).

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 diacids and other SOA components may 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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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 ($\omega C2$), 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

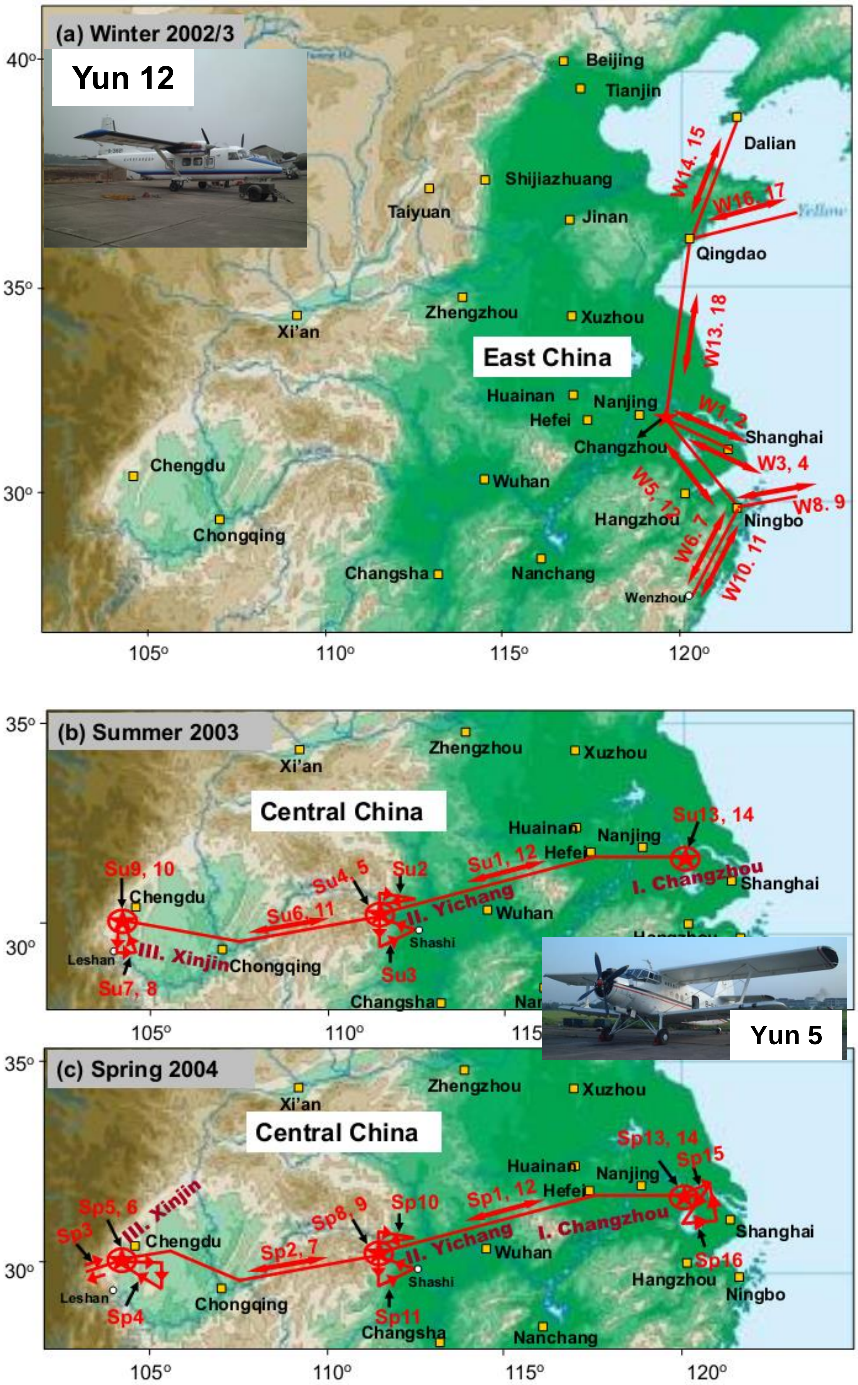

Figure 1. Tracks of research flights during aircraft measurements over China during (a) winter 2002, (b) summer 2003 and (c) spring 2004. The detailed sampling information with flight No. is listed in the Supplementary Table S1. The maps with the flight tracks were drawn by the software of PowerPoint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

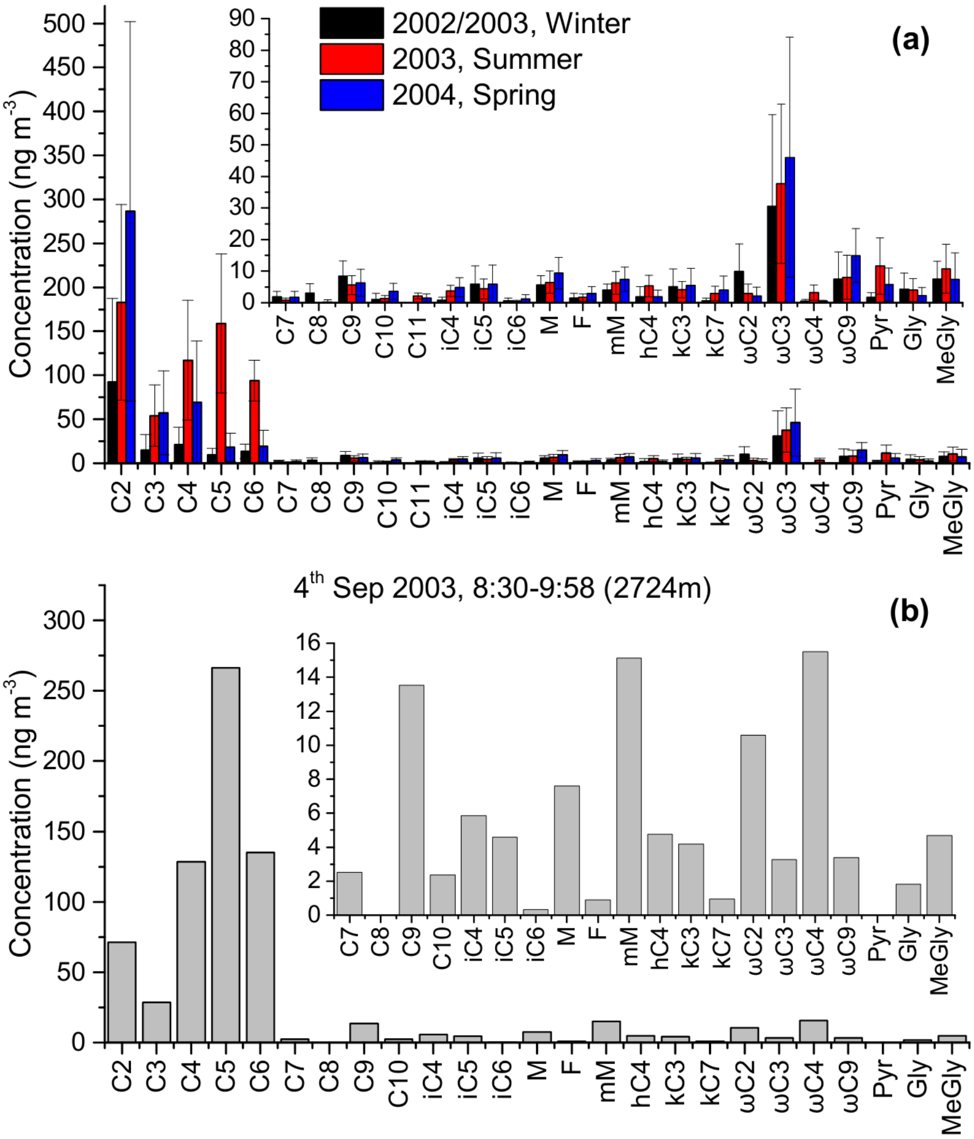

Figure 2. Molecular distributions of straight chain diacids (C_2–C_{11}), branched chain diacids (iC_4-iC_6), unsaturated diacids (M, F and mM), multifunctional diacids (hC_4, kC_3 and kC_7), ketoacids (ωC_2-ωC_4, ωC_9, and Pyr), and α-dicarbonyls (Gly and MeGly) in aircraft measurement over China; (a)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

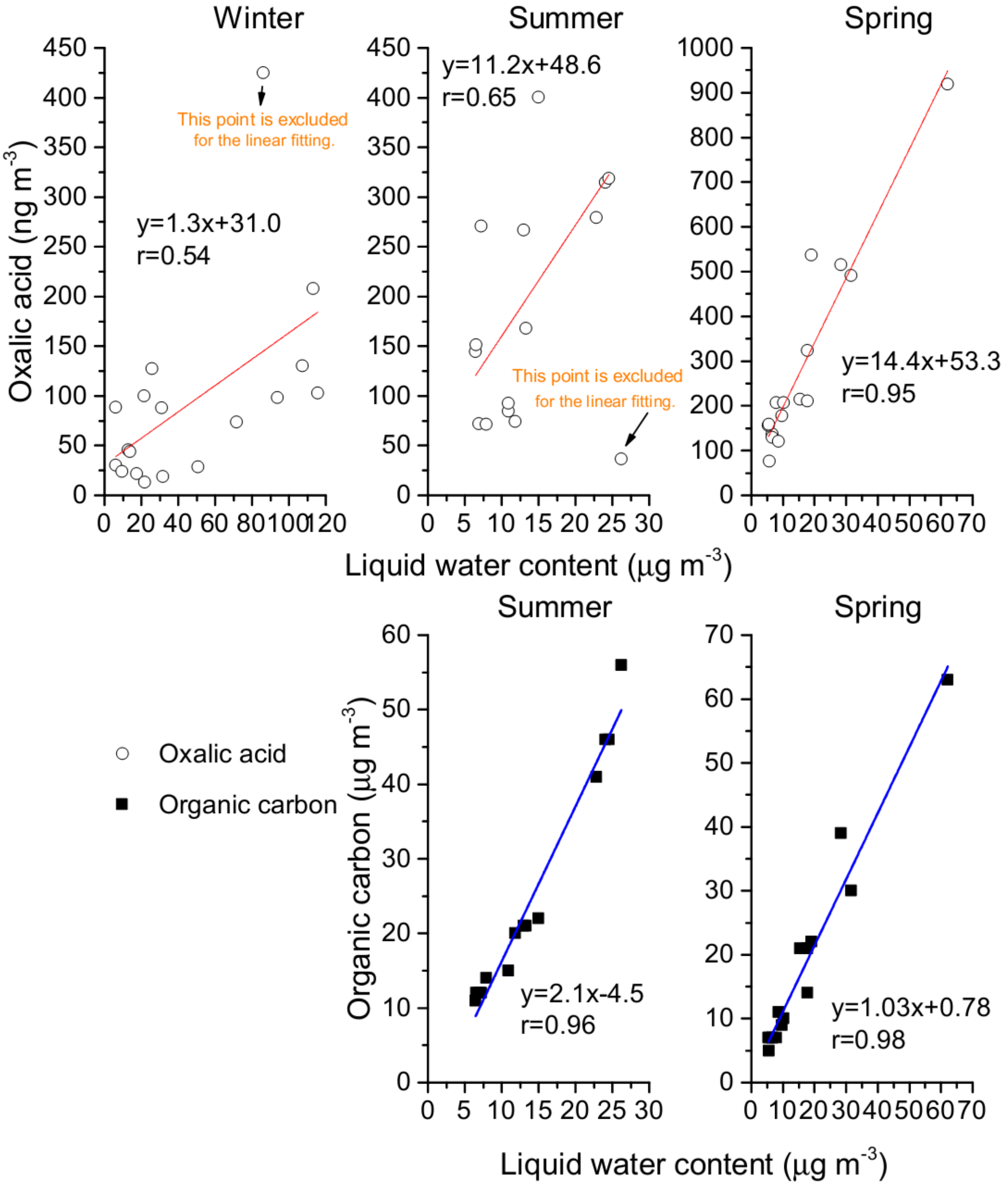

Figure 3. The linear fitting of the predicted liquid water content with organic carbon (OC) and oxalic acid aerosols during winter, summer, and spring aircraft measurements over China.

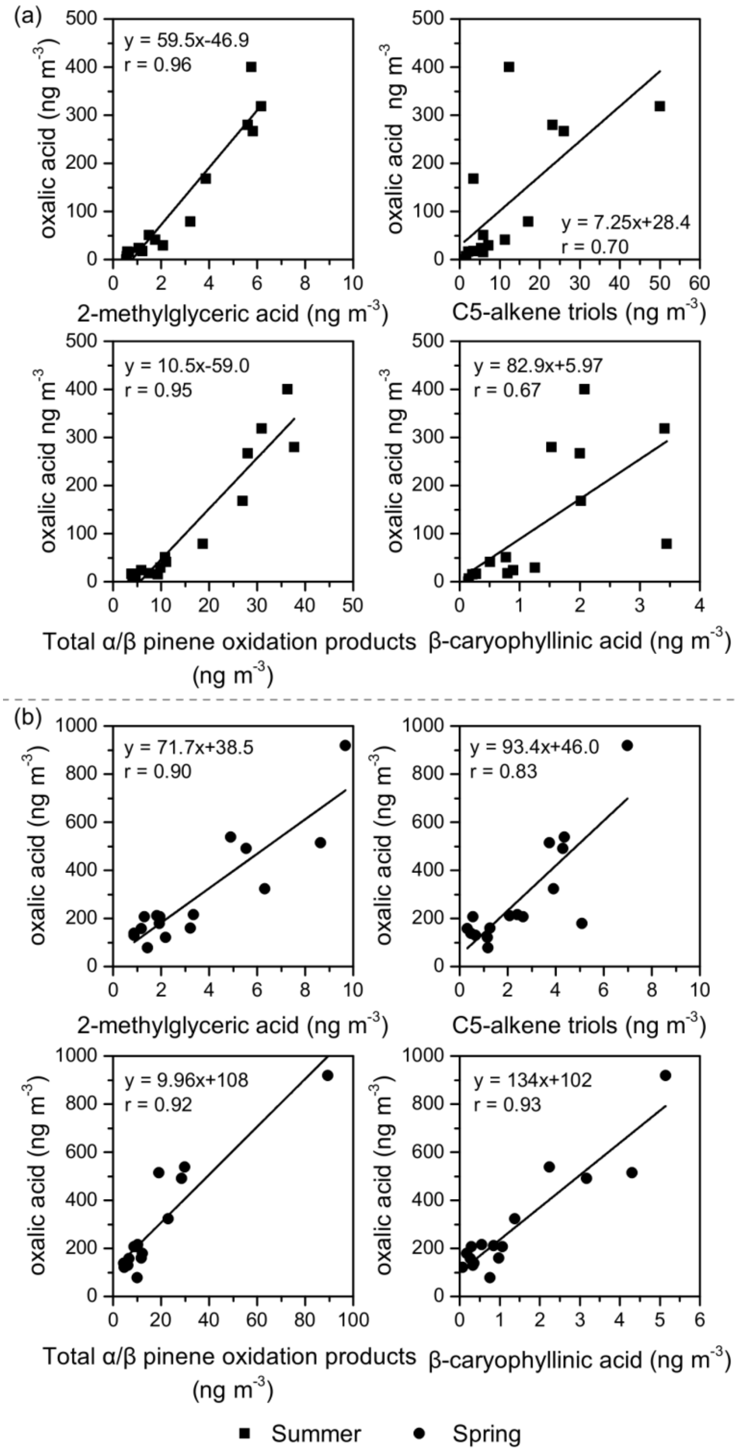

Figure 4. Linear relationship of the concentrations of oxalic acid with the detected tracer compounds for secondary organic aerosols (SOA) such as isoprene SOA tracers such as 2-methylglyceric acid and C5-alkene triols (sub-total of cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene,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

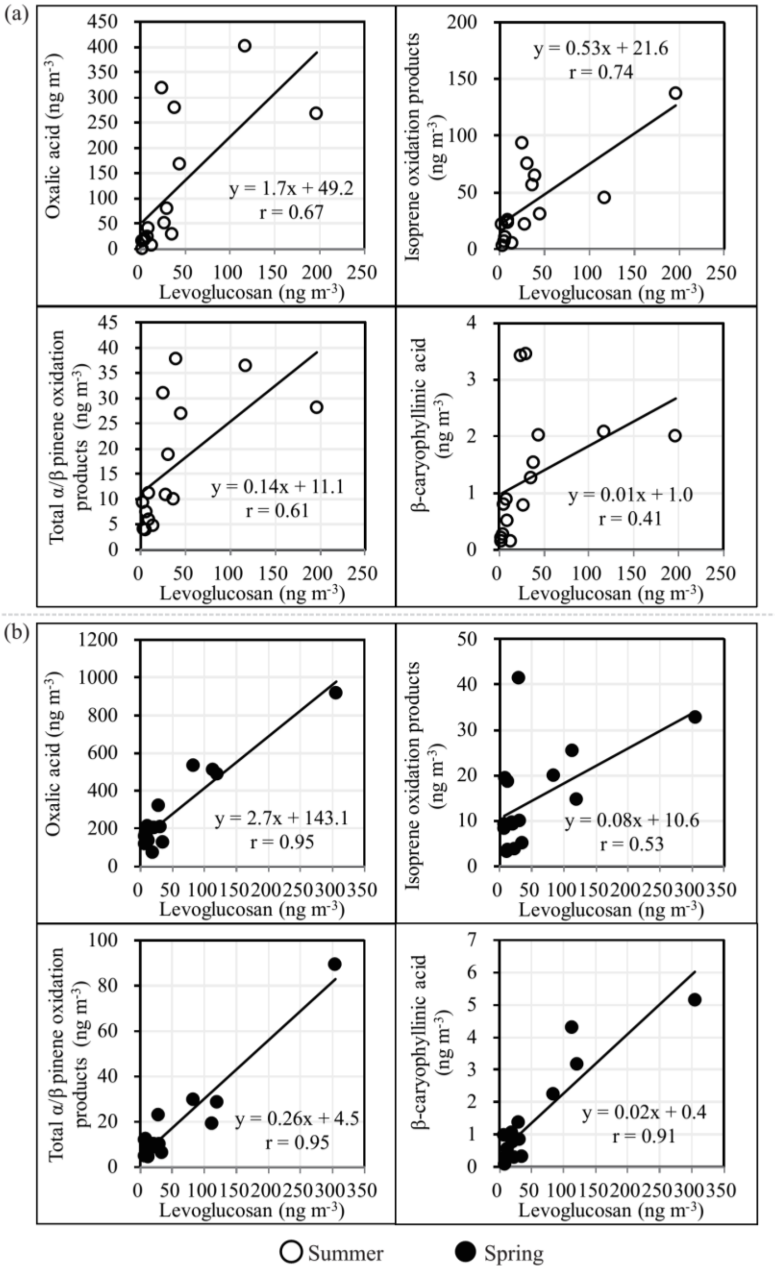

Figure 5. Linear relationship for the concentrations of levoglucosan with oxalic acid, isoprene SOA tracers, α/β-pinene SOA tracers and β-caryophyllene SOA tracer from the aircraft measurements over China during (a) summer and (b) spring.

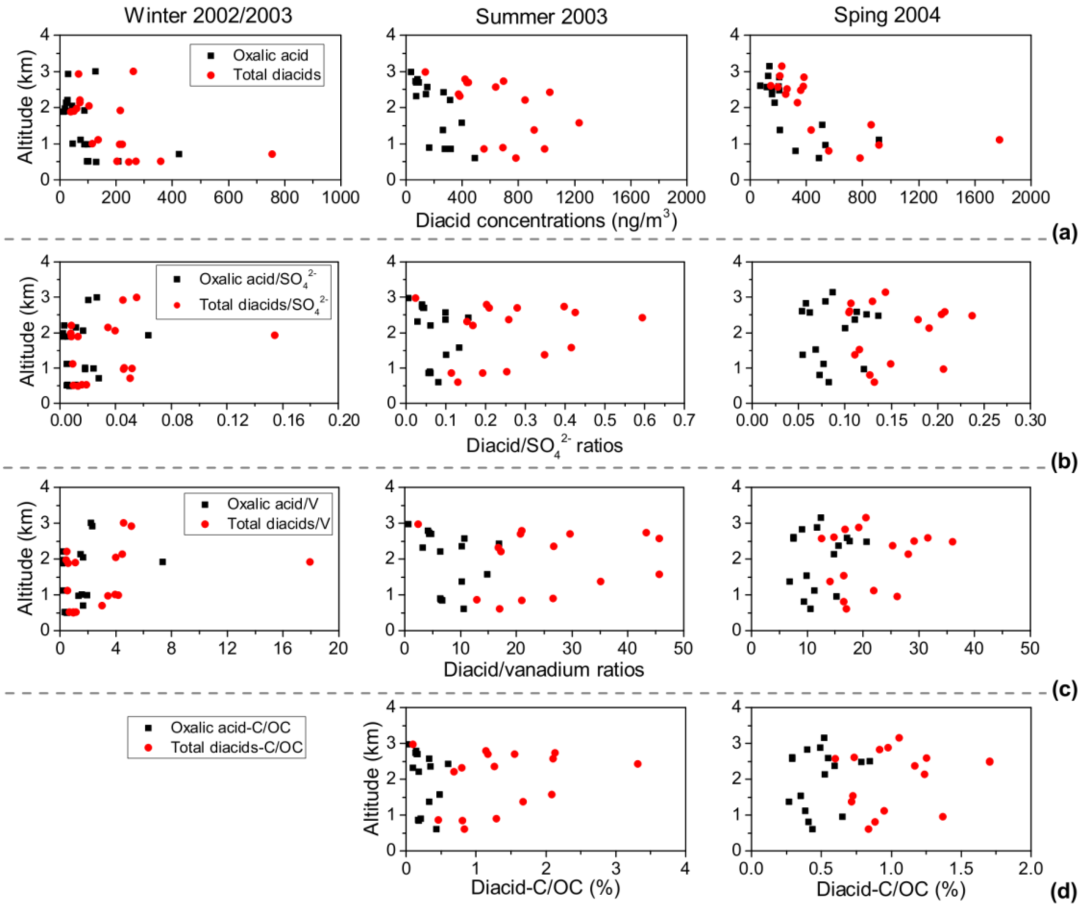

Figure 6. Vertical profiles of (a) concentrations of oxalic acid and total diacids, and their relative abundance to (b) sulfate (SO_4^{2-}), (c) vanadium (V), and (d) organic carbon (OC, %) in aerosol samples collected during winter 2002 (left), summer 2003 (middle) and spring 2004 (right) aircraft campaigns over China.