A sub-decadal trend of diacids in atmospheric aerosols in East Asia

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Abstract. The change of secondary organic aerosols (SOA) has been predicted to be highly uncertain in the future atmosphere in Asia. To better quantify the SOA change, we examine the sub-decadal (2001-2008) trend of major surrogate compounds (C_2 - C_{10} diacids) of SOA in atmospheric aerosols from the Gosan site on Jeju Island, South Korea. Gosan site is influenced by pollution-outflows from East Asia. The molecular distributions of diacids were characterized by the predominance of oxalic (C_2) acid followed by malonic (C_3) and succinic (C_4) acids in each year. The seasonal variations of diacids in each year were characterized by the highest concentrations of saturated diacids in spring and unsaturated diacids in winter. The consistent molecular distributions and seasonal variations along with significantly similar air mass transport patterns are indicative of similar pollution sources for diacids in East Asia over a sub-decadal scale. However, the intensity of the pollution sources has increased as evidenced by the increases of major diacids at the rate of 3.9 - 47.4% per year particularly in April. The temporal variations of atmospheric tracer compounds (carbon monoxide, levoglucosan, 2-methyltetrols, pinic acid, glyoxylic acid, glyoxal and methylglyoxal) suggest that the increases of diacids are due to the enhanced precursor emissions associated with more anthropogenic than biogenic activities followed by their chemical processing in the atmosphere. The trends of diacids are opposite to the reported decreases of sulfate, nitrate and ammonium in the recent years in East Asia. This study demonstrates that recent pollution control strategies in East Asia could not decrease organic acidic species in the atmosphere. The increases of water-soluble organic acid fraction could modify the aerosol organic composition and its sensitivity to climate relevant physical properties.

1 Introduction

Organic carbon (OC) can account for ~15 - 25% of aerosol mass in PM_{10} atmospheric particles (Boucher et al., 2013) and ~10 - 60% of aerosol mass in non-refractory PM_1 atmospheric particles (Zhang et al., 2007). These contributions are comparable to those of other major aerosol components including dust, sulfate, nitrate and ammonium (Zhang et al., 2007; Boucher et al., 2013). Source attribution studies have estimated up to 80% of OC as secondary in atmospheric aerosols (Zhang et al., 2007; Offenberg et al., 2007; Hallquist et al., 2009; Ding et al., 2012). The budget of global secondary organic aerosols (SOA), derived from the oxidation of volatile organic compounds (VOCs), is higher than that of global primary organic aerosols (POA) (Hallquist et al., 2009). The SOA can modulate water-uptake behavior of atmospheric aerosols (Swietlicki et al., 2008; Hong et al., 2014) and have adverse impacts on human health (Nawrot et al., 2007; Hallquist et al., 2009).

Although there are some primary sources of low-molecular-weight diacids having carbon numbers of 2-10 (Kawamura and Kaplan, 1987; Schauer et al., 1999, 2001), they are overwhelmingly generated in the atmosphere (Kalberer et al., 2000; Warneck, 2003; Fisseha et al., 2004; Tedetti et al., 2007; Kundu et al., 2010a; Charbouillot et al., 2012). For example, <1% of oxalic acid has been estimated to be emitted from the primary sources whereas the remaining part has been calculated to form in the aqueous-phase from precursors (e. g., glyoxal, methylglyoxal and glyoxylic acid) derived by the oxidation of biogenic and anthropogenic VOCs (Myriokefalitakis et al., 2011). Oxalic acid, the most abundant species of the diacids, can account for as much as half of the global SOA budget (Hallquist et al., 2009; Myriokefalitakis et al., 2011). Low-molecular-weight diacids have been ubiquitously detected in atmospheric aerosols, accounting for up to 20% of the water-soluble carbonaceous fraction of atmospheric aerosols (Kawamura and Sakaguchi, 1999; Kerminen et al., 1999; Decesari et al., 2006). These contributions are higher than those of known major

SOA tracers from biogenic and anthropogenic VOCs (Kleindienst et al., 2007; Stone et al., 2010; Fu et al., 2014). Thus, diacids are important surrogates of SOA in the atmosphere due to their ubiquity, secondary nature, and high contributions to SOA mass. In addition, diacids impart acidity to atmospheric aerosols (Myriokefalitakis et al., 2011). Diacids could be good indicators for evaluating the changes of SOA concentrations and their composition and physical properties in the future atmosphere.

Chemistry-transport models have predicted that the global SOA net production may change from 0.4% to 214% by the end of 21st century compared to that in 1990/2000 (Naik et al., 2004; Liao et al., 2006; Tsigaridis and Kanakidou, 2007; Heald et al., 2008). These large uncertainties are due to those associated with the predicted climate scenarios and various components of global atmosphere-land models. For example, there are 40 SRES (Special Report on Emission Scenarios) scenarios, which have resulted in carbon dioxide emissions in the range of 3.3 to 37 GtC/yr by the end of 2100 (Nakicenovic et al., 2000) and isoprene emissions have been projected to increase in the range of 500-1000 Tg (Levis et al., 2003; Tao and Jain, 2005; Guenther et al., 2006). Due to a large uncertainty in the projection of SOA using the models, long-term observations of major surrogates (e.g., diacids) of SOA are required for better understanding the changes of SOA in the coming years.

Due to the importance of diacids as a pool of SOA, we study their long-term (2001-2008) trends in atmospheric aerosol samples (the number of samples, n = 718) collected at Gosan site in Jeju Island, South Korea. Gosan is heavily influenced by pollution-outflows from East Asia. Therefore, any change in the abundances of diacids will reflect the alteration of the pollution sources and atmospheric chemical processes in East Asia. East Asia is of particular importance because the chemistry-climate model has predicted the highest increases of SOA abundances in the future Asian atmosphere (Heald et al., 2008). A sub-decadal trend obtained from this study could be used as a reference to evaluate the alteration of composition and physical properties of SOA in the future atmosphere in East Asia.

2 Experimental Section

2.1 Site description

The Gosan site on Jeju Island (33°29′ N, 126°16′ E) is situated at the boundary of the Yellow Sea and East China Sea (Fig. 1). The site is ~100 km south of the Korean Peninsula, ~500 km east of China (Jiangsu province or Shanghai), ~200 km west of Kyushu Island, Japan, and ~1000 km northeast of Taipei. The Gosan site is located on the western edge of Jeju Island, which is isolated from residential areas on the island and the surroundings are covered with grasses (Kundu et al., 2010c). Due to its location and very limited local anthropogenic emissions, Gosan has been considered as an ideal site to monitor the outflows from East Asia (Kundu et al., 2010c).

2.2 Aerosol sampling

Atmospheric total suspended particles (TSP) samples (n = 714) were collected at Gosan over 6 hours to 7 days throughout the years from April 2001 to November 2008. The total number of samples collected were 71 in 2001, 25 in 2002, 48 in 2003, 98 in 2004, 123 in 2005, 116 in 2006, 142 in 2007, and 91 in 2008. Due to various technical problems, aerosol samples could not be collected on January - March 2001; April - December 2002; January - March 2003; July - August 2005; September - October 2006; and May and December 2008. Aerosol samples were collected onto pre-combusted (500°C) quartz fiber filters (20 × 25 cm, Pallflex 2500 QAT-UP) using a high volume air sampler (Kimoto AS-810) installed on the roof of a trailer house (~3 m above the ground). The flow rate was maintained at 0.8 m^{-3} min^{-1}. Prebaked glass jars (150 ml) with a Teflon-lined screw cap were used to store the filters before and after the sampling. Samples were kept in a freezer after the collection, transported to our laboratory at ambient temperatures, and then again kept in a dark freezer room at -20

°C until analysis. Field blank filters were collected periodically by setting the filter substrates on the filter cartridge at Gosan; however, air was not passed through the filter.

2.3 Analytical method

Aerosol samples were analyzed for diacids (C_2 - C_{10}), oxoacid (glyoxylic acid) and α-dicarbonyls (glyoxal and methylglyoxal) using a method described elsewhere (Kawamura, 1993). Briefly, target analytes were isolated by the extraction of aliquots of filter samples with water (5 ml × 3, >18 MΩ) under ultrasonic agitation. The aerosol extract was filtered to remove filter debris and insoluble particles using a glass column (Pasteur pipette) packed with quartz wool. Aerosol extracts were evaporated to almost dryness using a rotary evaporator (~40 °C) under vacuum. The target analytes then were derivatized with 14% borontrifluoride in n-butanol at 100 °C over an hour. Water and hexane were simultaneously added to isolate derivatized esters and acetals from polar compounds. Esters and acetals partitioned into n-hexane whereas inorganic materials such as boric and fluoric acids were dissolved into water. The hexane layer was separated and completely dried using a rotary evaporator under vacuum and nitrogen (N_2) blow-down technique. Then, the esters and acetals of target analytes were dissolved in a known volume of n-hexane.

A 2 μl aliquot of the sample was injected into a capillary gas chromatograph (GC, Hewlett-Packard, HP6890) equipped with a split/splitless injector, fused silica capillary column (HP-5, 25 m long × 0.2 mm id × 0.5 μm film thickness) and flame ionization detector (FID). The GC oven temperature was maintained at 50 °C for 2 min, ramped at 30 °C/min to 120°C, then at 6°C/min to 310 °C, and held for 10 min. Peaks on the GC chromatograms were identified with reference to the authentic standard's retention times obtained by GC-FID and mass spectra acquired using a mass spectrometer (MS) (Thermoquest, Trace MS). The concentrations were calculated in terms of the peak area of authentic dibutyl succinate.

Free diacids were spiked onto pre-combusted quartz fiber filters and analyzed like real samples to test the recovery. The recoveries were found as 80-85% for oxalic acid and above 90% for malonic, glutaric, succinic, and adipic acids. The recoveries of glyoxylic acid, glyoxal, and methylglyoxal have been reported to be 88%, 91% and 47%, respectively (Kawamura et al., 2013). Replicate analyses of aerosol samples showed that the analytical error of this method was less than 10% for major species reported in this study. Field blanks showed small peaks of oxalic, succinic, adipic, and phthalic acids and methylglyoxal. However, their levels were very low (0.1-3%) compared to those of the real samples. The reported concentrations have been corrected for the field blanks, but not for recoveries.

Levoglucosan (a biomass burning tracer), 2-methyltetrols (isoprene derived SOA tracers) and pinic acid (α-pinene derived SOA tracer) were determined in aerosol samples collected from 2003-2004 using a GC-MS instrument. The detailed analytical protocols have been described elsewhere (Fu et al., 2014). Total carbon (TC) was measured using an elemental analyzer (EA; model: NA 1500 NCS, Carlo Erba Instruments) for aerosol samples collected over 2001-2006 following the method described elsewhere (Kundu et al., 2010b). A small disc (area 2.54 cm^2) of each filter sample was wrapped with a cleaned tin cup using tweezers and then introduced into the EA using an autosampler. The samples were burned in the presence of pure oxygen in a combustion column packed with chromium trioxide at 1020 °C. The derived carbon dioxide (CO_2) was separated on a gas chromatograph (GC) installed within the EA instrument and then measured with a thermal conductivity detector. The concentrations of O_3 and CO were measured by the Korea Meteorological Administration (KMA) using Thermo Environmental Instrument 49C and 48C, respectively (Thermo Inc., USA).

3 Results and Discussion

3.1 Interannual variations in the molecular distributions of diacids

Molecular distributions, related to the presence/absence and abundance of organic compounds in atmospheric aerosols, provide important information about their sources, formation, chemical evolution and physical properties (Hallquist et al., 2009). Lower- (C_2 - C_6) and higher- (C_7 - C_{10}) molecular-weight normal-chain diacids, branched-chain diacids (C_4 - C_6), multi-functional diacids (C_3 - C_7), and unsaturated diacids (C_4 - C_8) were detected in this study. Table 1 presents their full and abbreviated names, and monthly concentrations (range and average) over the time period of 2001-2008.

The molecular distributions are discussed here based on the monthly median concentrations of the individual years. Oxalic (C_2) acid was found as the most abundant species followed by either malonic (C_3) acid or succinic (C_4) acid among all detected diacids in every month of the studied years (2001 - 2008). The fourth, fifth and sixth abundant diacids were highly variable with the predominance of glutaric (C_5), adipic (C_6), azelaic (C_9), malic (hC_4), terephthalic (tPh), or phthalic (Ph) acids. Similar types of molecular distributions have also been reported in atmospheric aerosols collected around the globe (Kawamura and Sakaguchi, 1999; Kerminen et al., 1999; Decesari et al., 2006; Kundu et al., 2010a; Kundu et al., 2010c; Kawamura et al., 2013). To explore interannual differences in the molecular distributions, the analysis of variance (ANOVA) was carried out by comparing the median concentrations of the similar months of 2001-2008. Significant ($p < 0.05$) differences in the molecular distributions of diacids were not observed among the studied years. Based on these results and similarity of mean air mass trajectory pathways among the identical months (exception: May, June, August and September) of 2001-2008 (as shown in Fig. 1a-d and Fig. S1a-h), we conclude that the sources of diacids mostly remain identical in East Asia over a sub-decadal scale.

3.2 Seasonal variations of diacids

Four seasons are defined in this study as follows: March - May as spring, June - August as summer, September - November as autumn and December - February as winter. Saturated- and multifunctional- diacids showed maxima in spring with comparable concentrations in autumn and winter (Fig. 2a-h and Fig. S2a-h). In contrast, unsaturated diacids, except for fumaric acid (F), showed maxima in winter (Fig. 3a-f and Fig. S3a-f). We discuss the observed seasonality in terms of air mass trajectory, primary and secondary pollution sources, meteorological parameters (boundary layer height, precipitation, temperature and humidity), and sink terms (oxidation by hydroxyl (OH) radicals and wet deposition).

Typical air mass transport patterns at Gosan have been shown with reference to the mid-month of each season over the time period of 2001-2008 (Fig. 1). The air mass transport patterns for the remaining have also been shown in Fig. S1. Maximum concentrations of saturated diacids in the spring months are due to polluted air mass transport at Gosan from East China (Fig. 1b), where the highest concentration of nitrogen dioxide (NO_2) has been spotted by satellite instruments (Richter et al., 2005). High concentrations of unsaturated diacids in the cold seasons (winter and autumn) coincide with the passage of air masses from North China (Fig. 1a, d). The consumptions of coal and biomass are significantly enhanced due to home heating in the cold seasons in North China (Kundu et al., 2010a). The low concentrations for all saturated and unsaturated diacids in summer are due to the transport of marine air parcels at Gosan. The marine air parcels are delivered to the Gosan site from the China Sea, Yellow Sea and western North Pacific in summer (Fig. 1c).

The seasonal distributions of saturated diacids are different from those of unsaturated diacids, suggesting that their sources could be season-specific. The highest concentrations of saturated diacids in spring overlap with the maxima of ozone (O_3) at Gosan (Fig. 4a) and its surrounding polluted regions in East Asia (Naja and Akimoto, 2004; Ohara et al., 2007; Xu et al., 2008; Wang et al., 2009), indicating an elevated production of diacids by atmospheric chemical processes. Previous studies reported that diacids in SOA were generated by the oxidation of anthropogenic (e.g., cyclohexene, 1, 3, 5-trimethylbenzene) and biogenic VOCs (e.g., isoprene) (Kalberer et al., 2000; Fisseha et al., 2004; Myriokefalitakis et al., 2011). Diacids with higher abundances have also been found in biomass-burning influenced aerosols (Kundu et al., 2010a; Myriokefalitakis et al., 2011; Kawamura et al., 2013). In 2003-2004 spring, major saturated diacids did not correlate or loosely correlated with 2-methyltetrols (isoprene-SOA tracers, $r^2 = 0.001\text{-}0.05$) (Fig. 5a-e), pinic acid (α-pinene-SOA tracer, 0.10-0.39) (Fig. 6a-e) and levoglucosan (biomass burning tracer, 0.001-0.07) (Fig. 7a-e) (e.g., Fu et al., 2014). The lack of correlations in spring could be related with more production of diacids from the oxidation of anthropogenic VOCs than those from the oxidation of biogenic VOCs and related biomass-burning derived precursors. This interpretation can be supported by the fact that concentrations of 2-methyltetrols and pinic acid in spring are 2.2 - 6.5 times lower than those in summer (Fig. 4b). In contrast, saturated diacids showed significant ($p < 0.05$) correlations in summer ($r^2 = 0.29 - 0.60$) and winter (0.47 - 0.66) with 2-methyltetrols (Fig. 5a-e), pinic acid (0.48 - 0.95 and 0.30 - 0.82, respectively) (Fig. 6a-e), and levoglucosan (0.38 - 0.70 and 0.35 - 0.72, respectively) (Fig. 7a-e). These results show that the oxidation of biogenic VOCs and biomass-burning derived-precursors are the dominant sources of diacids in summer and winter.

The seasonal variations of unsaturated diacids are similar with those of levoglucosan (biomass burning tracer) and CO (combustion tracer) (Fig. 4c, d). Tight correlations ($r^2 = 0.61\text{-}0.76$) were obtained between the major unsaturated diacids and levoglucosan in winter at the 95% confidence level (Fig. 7f-g). These correlations were reduced to 0.39-0.64 in summer and 0.42-0.54 in autumn (Fig. 7f-g), suggesting that biomass burning-derived precursors are the most intense sources of unsaturated diacids in winter followed by summer and fall. There are no correlations between unsaturated diacids and levoglucosan in spring, further suggesting that biomass burning derived precursors are not an important source of diacids in spring in East Asia. Aliphatic unsaturated diacids including maleic (M), fumaric (F) and methylmaleic (mM) acids are significantly ($p < 0.05$) correlated in summer (r^2 = 0.40-0.52) and winter (r^2 = 0.57-0.60) with 2-methyltetrols (Fig. 5f) and pinic acid (0.90-0.91 and 0.41-0.71, respectively) (Fig. 6f). These results show that there is a strong link between aliphatic unsaturated diacids and biogenic VOCs.

Total carbon (TC) normalized concentrations of saturated diacids showed higher values in spring and lower values in winter like the absolute concentrations; however, a peak emerged in summer (Fig. S4a-h). These results show that the dilution of the atmosphere does not affect the spring maxima, but summer concentrations are decreased by atmospheric dilution mainly due to the transport of clean air masses from the oceans. The seasonality of TC-normalized concentrations of unsaturated diacids was characterized with winter maxima, being similar to the seasonality of their absolute concentrations in winter (Fig. S5a-f). These results indicate that a shrink of the boundary layer had no effect on the winter maxima. Aerosol liquid water content and aerosol composition are not expected to drive the seasonality of diacids as an insignificant amount (<5% of global budget) of oxalic acid has been estimated to be generated in aqueous aerosols (Myriokefalitakis et al., 2011).

About 62% and 34% of the global budget of oxalic acid and potentially other diacids are removed from the atmosphere by wet deposition and oxidation by OH radicals, respectively (Myriokefalitakis et al., 2011). Therefore, less precipitation (Fig. S6a) and OH radical concentrations in winter may have an effect on the winter maxima of unsaturated diacids. However, this effect should not be dominating over the major factors (e.g., sources and air mass transport) because of the observed peak maxima of saturated diacids in spring when high amount of precipitation has been observed (Fig. S6a) and higher OH radical concentrations are expected than those in winter (Kanaya et al., 2007). Temperature and relative humidity showed the highest values in summer followed by spring and the cold seasons (winter and autumn) at Gosan (Fig. S6b, c), however they are not expected to affect seasonality via the partitioning because of the predominant existence of diacids in aerosol-phase (Mochida et al., 2003). In conclusion, the seasonal cycles of saturated and unsaturated diacids at Gosan are mostly likely determined by air mass pathways associated with their pollution sources in East Asia. The minor parameters in determining the seasonality at Gosan are meteorological parameters and sink terms.

3.3 Interannual variability of diacids

Figure 8 shows year-to-year variations of the major saturated (Fig. 8a-f) and unsaturated (Fig. 8g, h) diacids for April during the time period of 2001-2008. Overall, diacid concentrations are observed to increase from 2001 to 2008 in April. The linear regression analysis, based on the least squares and median and percentile (25th and 75th) concentrations, shows a clear increasing trend with 3.9 - 47.4% per year ($r^2 = 0.38 - 0.94$, $p < 0.051$) in April. Significant ($p < 0.05$) enhancements are occasionally observed in other spring and winter months (Table S1); however, the increases are not significant ($p > 0.05$) in autumn and summer months (Table S1). The interannual variations are interpreted by considering a number of factors including yearly behavior of CO, O_3, VOCs and their oxidation products (glyoxylic acid, glyoxal and methylglyoxal), biogenic (azelaic acid) and anthropogenic (phthalic acids) tracers. We do not observe any significant variability of air masses during the study period of 2001-2008 (Fig. 3), showing that the variability of air masses does not affect the interannual increases of the diacids.

An increase of CO at Gosan has not been observed in April over the time period of 2001-2008 (Fig. 9a). We also found the absence of correlations between diacids and levoglucosan in April as discussed previously. These results show that direct emissions from combustion sources did not cause the yearly increases of saturated and unsaturated diacids. Instead, atmospheric chemical processes could be responsible for their increases in April on a sub-decadal scale. The increases of both O_3 and VOCs have been reported at several sites in China, Japan and Korea (Naja and Akimoto, 2004; Ohara et al., 2007; Xu et al., 2008; Wang et al., 2009; Fu and Liao, 2012), which may enhance atmospheric chemical processes resulting in the production of diacids in the atmosphere. This explanation can be supported by the increases of glyoxylic acid and glyoxal (Fig. 9b, c), which are the oxidation products of major anthropogenic and biogenic VOCs and intermediates for the production of oxalic acid via aqueous-phase reactions (Myriokefalitakis et al., 2011).

Significant ($p < 0.05$) increases of CO from 2001 to 2008 have been observed in the months of winter (except for February) and autumn (except for October) during the study period (Table S2), which could have been associated with the increases in the emissions of VOCs. However, systematic annual increases in diacids (Table S1) and precursors of oxalic acid (glyoxylic acid, glyoxal and methylglyoxal) (Table S2) were not observed in the months of autumn and winter, suggesting that oxidant concentrations in the cold seasons are not high enough to convert the increased VOCs to diacids. The lack of annual increases of diacids and their precursors in the summer months are indicative of no changes in the emissions of oceanic VOCs and the subsequent chemical processing in the atmosphere.

It is very important to understand whether the atmospheric chemical processing of anthropogenic or biogenic VOCs is causing the increases in the concentrations of diacids in the atmosphere. Phthalic and adipic acids have been reported to form by the oxidation of anthropogenic VOCs (Kalberer et al., 2000; Fisseha et al., 2004) whereas azelaic acid is produced via the oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987; Tedetti et al., 2006). We have observed the increases of both anthropogenic (phthalic acids and adipic acid) and biogenic (azelaic acid) diacids (Fig. 8), demonstrating that both biogenic and anthropogenic VOCs are causing the April increases of diacids in the atmosphere. Indeed, the increases of biogenic and anthropogenic VOCs have been reported in East Asia during our study period (Ohara et al., 2007; Fu and Liao, 2012). However, tighter yearly increases of anthropogenic diacids than biogenic diacids (see Fig. 8) are indicative of more influences of anthropogenic VOCs in driving the interannual increases of diacids in East Asia. The higher influences of anthropogenic VOCs than biogenic VOCs can also be evidenced in the lack of correlations between diacids and SOA tracers (2-methyltetrols and pinic acid) in spring as discussed previously. The absence of any increase of methylglyoxal (Fig. 9d), which is an oxidation product of isoprene and 80% of which has been reported to be generated from the oxidation of isoprene in the atmosphere (Myriokefalitakis et al., 2011), further supports the lesser influence of biogenic VOCs on increased diacids.

4 Conclusions and Atmospheric Implications

The seasonal variations in the pollution sources of diacids, an important fraction of organic aerosols (OA), remain identical over a sub-decadal scale in East Asia. But, the strength of their pollution sources has increased from 2001 to 2008, which is evidenced by the increases in the loadings of diacids in atmospheric aerosols. The month-specific interannual increases show that this required not only an enhanced emission of anthropogenic and biogenic VOCs but also their efficient chemical processing to increase the loadings of diacids in the atmosphere. The increases of diacids derived from anthropogenic VOCs are more prominent than those of diacids generated from biogenic VOCs in East Asia. The increases of water-soluble organic acid fraction could modify the aerosol organic composition and its sensitivity to climate relevant physical properties.

Atmospheric pollution control strategies in East Asia have successfully decreased the loading of inorganic acidic (sulfate and nitrate) and basic (ammonium) species in recent years

(2007-2012) (Boreddy and Kawamura, 2015). However, this study demonstrates that recent pollution control strategies in East Asia could not decrease organic acidic species in the atmosphere. The increase of diacids in atmospheric aerosols could still maintain aerosol acidity although inorganic acidic species are decreasing. Aerosol acidity has been shown to increase aerosol yields in the atmosphere (Surratt et al., 2010). Since diacids are water-soluble in nature, their increases will modify the water-uptake activities of atmospheric aerosols, which will have subsequent influences on the direct and indirect climate effects of atmospheric aerosols.

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Table 1. Monthly concentrations (range and average) of diacids in atmospheric aerosols (n = 718) collected from 2001 - 2008 at Gosan, Jeju Island, South Korea.

Organic Compounds	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Normal Chain Saturated Diacids												
Oxalic, C_2	67-2491 (395)	95-908 (358)	1-1196 (448)	98-2088 (558)	198-1265 (619)	174-1437 (517)	87-973 (323)	21-1408 (240)	88-782 (325)	126-1421 (503)	111-861 (403)	71-1251 (291)
Malonic, C_3	8-212 (41)	10-128 (42)	0.2-138 (55)	10-168 (72)	12-166 (81)	15-193 (77)	9-118 (47)	2-192 (39)	10-135 (51)	23-150 (65)	14-114 (47)	8-129 (30)
Succinic, C_4	6-205 (40)	6-130 (38)	0.2-153 (52)	10-216 (66)	8-195 (78)	11-251 (68)	3-221 (32)	2-105 (17)	3-71 (24)	12-152 (48)	14-155 (42)	8-118 (28)
Glutaric, C_5	2-62 (11)	2-27 (10)	0.1-33 (12)	0-72 (15)	1-64 (17)	1-69 (11)	0.3-37 (5)	0.1-11 (3)	0.7-14 (5)	2-32 (11)	2-36 (10)	2-41 (8)
Adipic, C_6	0.9-37 (6)	2-13 (5)	0.03-20 (6)	0.2-37 (7)	0.7-19 (7)	0.6-27 (4)	0.09-24 (2)	0.2-11 (1)	0.2-7 (2)	0.9-18 (5)	1-12 (5)	0.4-18 (4)
Pimelic, C_7	0.2-19 (3)	0.4-10 (2)	0.01-10 (3)	0-13 (3)	0.2-8 (3)	0.1-9 (2)	0-3 (0.7)	0.04-2 (0.5)	0.1-3 (1)	0.7-9 (2)	0.5-7 (2)	0.4-11 (2)
Suberic, C_8	0-14 (2)	0-4 (1)	0-7 (2)	0-10 (2)	0-6 (2)	0-8 (1)	0-5 (0.8)	0-4 (0.6)	0-3 (0.9)	0-5 (1)	0-4 (1)	0-9 (1)
Azelaic, C_9	0.8-23 (5)	0.8-21 (4)	0.02-19 (4)	0-15 (5)	0.7-11 (5)	0-15 (4)	0.4-8 (3)	0.2-20 (3)	1-6 (4)	1-7 (4)	0.5-15 (4)	0.9-13 (3)
Sebacic, C_{10}	0-5 (0.7)	0-2 (0.5)	0-2 (0.7)	0-5 (1)	0-2 (1)	0-2 (0.6)	0-0.8 (0.2)	0-4 (0.4)	0-2 (0.3)	0.1-2 (0.7)	0-3 (0.6)	0-3 (0.5)
Branched Chain Saturated Diacids												
Methylmalonic, iC_4	0.2-5 (1)	0.2-2 (1)	0.01-5 (1)	0-5 (1)	0.2-5 (1)	0-5 (1)	0-5 (0.9)	0.1-5 (0.8)	0.2-3 (1)	0.7-4 (2)	0.2-3 (1)	0.2-4 (0.9)
Methylsuccinic, iC_5	0.8-35 (5)	1-19 (5)	0.02-16 (6)	0.8-19 (5)	0.6-13 (5)	0.4-11 (3)	0.2-10 (2)	0.04-5 (0.9)	0.09-4 (1)	0.6-12 (4)	1-12 (4)	1-12 (4)
Methylglutaric, iC_6	0.3-7 (1)	0.3-3 (1)	0.01-5 (1)	0.2-4 (1)	0.1-5 (1)	0.03-5 (0.7)	0-2 (0.3)	0-1 (0.2)	0-1 (0.3)	0-2 (0.8)	0.2-2 (0.9)	0.3-3 (0.9)
Multifunctional Saturated Diacids												
Hydroxysuccinic, hC4	0-48 (4)	0-34 (4)	0-47 (6)	0-77 (7)	0-45 (7)	0-80 (7)	0-32 (2)	0-5 (0.4)	0-3 (0.7)	0-15 (2)	0-10 (2)	0-12 (1)
Ketomalonic, kC_3	0.1-24 (4)	0.1-16 (3)	0-13 (3)	0-15 (3)	0-8 (2)	0-6 (1)	0-2 (0.4)	0.05-10 (0.7)	0-4 (0.8)	0.4-9 (2)	0.09-10 (2)	0.2-11 (2)
Ketopimelic, kC_7	0-10 (2)	0.3-5 (2)	0.01-10 (3)	0.01-23 (5)	0.6-20 (7)	0.2-25 (6)	0.07-14 (2)	0.04-7 (1)	0.1-8 (2)	0.5-8 (4)	0.3-7 (2)	0-5 (1)
Unsaturated Dicacids												
Maleic, M	1-54 (7)	2-44 (6)	0.06-32 (5)	0.2-14 (5)	0.06-13 (4)	0.2-9 (3)	0.2-8 (1)	0.1-7 (0.9)	0.3-6 (1)	1-8 (3)	1-9 (4)	0.4-14 (5)
Fumaric, F	0.7-25 (4)	0.7-13 (3)	0.02-12 (3)	0.5-14 (5)	0.4-9 (4)	0.3-10 (3)	0-6 (1)	0.05-5 (0.8)	0.3-5 (1)	0.5-9 (3)	0.7-6 (3)	0.7-12 (3)
Methylmaleic, mM	0.9-39 (5)	0.7-25 (4)	0.02-21 (4)	0.3-22 (4)	0.2-9 (3)	0-10 (2)	0-8 (1)	0.08-4 (0.7)	0-5 (1)	0-13 (3)	0-8 (3)	0.9-14 (3)
Phthalic, Ph	5-230 (29)	5-59 (19)	0.1-50 (15)	0.9-60 (12)	0.2-27 (8)	0.05-16 (5)	0-18 (3)	0.3-24 (3)	0.1-12 (4)	2-28 (9)	2-51 (17)	5-64 (19)
Isophthalic, iPh	0-11 (2)	0.3-11 (2)	0-7 (2)	0-9 (1)	0.02-5 (1)	0-4 (0.7)	0-3 (0.2)	0-2 (0.2)	0-2 (0.4)	0-4 (1)	0.1-9 (1)	0-5 (1)
Terephthalic, tPh	2-71 (10)	2-26 (8)	0-38 (8)	0.4-41 (9)	0.01-22 (7)	0.7-18 (6)	0.2-15 (4)	0.1-33 (4)	0.7-14 (5)	2-16 (8)	3-15 (8)	2-29 (8)

Note: "0" means below detection limit (BDL). The aerosol samples collected were 64 in January, 51 in February, 86 in March, 87 in April, 62 in May, 54 in June, 42 in July, 66 in August, 44 in September, 53 in October, 52 in November and 57 in December.

Figure Captions

Fig. 1. Map showing the Gosan site (star symbol) on Jeju Island, South Korea along with the monthly averaged air mass backward trajectories for the time period of 2001-2008. (a) January, (b) April, (c) July and (d) October. Backward trajectories were calculated using the NOAA HYSPLIT model at 500 m above ground level over 5 days.

Fig. 2. Seasonal variations of selected saturated and multifunctional diacids including oxalic (a, b), azelaic (c, d), methylsuccinic (e, f) and ketopimelic (g, h) acids in ambient aerosol samples. The right panels are drawn based on the monthly binned concentrations irrespective of the years. The lower and upper whiskers represent the 10th and 90th percentiles, respectively. The outliers are excluded in the right panels to avoid any distortion in the seasonality.

Fig. 3. Seasonal variations of selected unsaturated diacids including maleic (a, b), phthalic (c, d) and terephthalic (e, f) acids in ambient aerosol samples. The right panels are drawn based on the monthly binned concentrations irrespective of the years. The lower and upper whiskers represent the 10th and 90th percentiles, respectively. The outliers are excluded in the right panels to avoid any distortion in the seasonality.

Fig. 4. Seasonal variations of chemical tracers in the atmosphere at Gosan. (a) ozone (O_3), (b) 2-methtyltetrols, (c) carbon monoxide (CO) and (d) levoglucosan. O_3 and CO data were obtained from the Korea Meteorological Administration (KMA). The insets in the left panel show the monthly averaged concentrations of O_3 and CO during time period of 2001-2008.

Fig. 5. Correlations of 2-methyltetrols (SOA tracers of isoprene) with saturated (a - e) and unsaturated (f - h) diacids in aerosol samples collected from 2003 April to 2004 April. (a) oxalic (C_2), (b) azelaic (C_9), (c) methylsuccinic (iC_5), (d) ketopimelic (kC_7), (e) ketomalonic (kC_3), (f) maleic (M), (g) fumaric (F) and (h) methylmaleic (mM) acids. Note that data have been segregated by the season.

Fig. 6. Correlations of pinic acid (a SOA tracer of α-pinene) with saturated (a - e) and unsaturated (f - h) diacids in aerosol samples collected from 2003 April to 2004 April. (a) oxalic (C_2), (b) azelaic (C_9), (c) methylsuccinic (iC_5), (d) ketopimelic (kC_7), (e) ketomalonic (kC_3), (f) maleic (M), (g) fumaric (F) and (h) methylmaleic (mM) acids. Note that data have been segregated by the season.

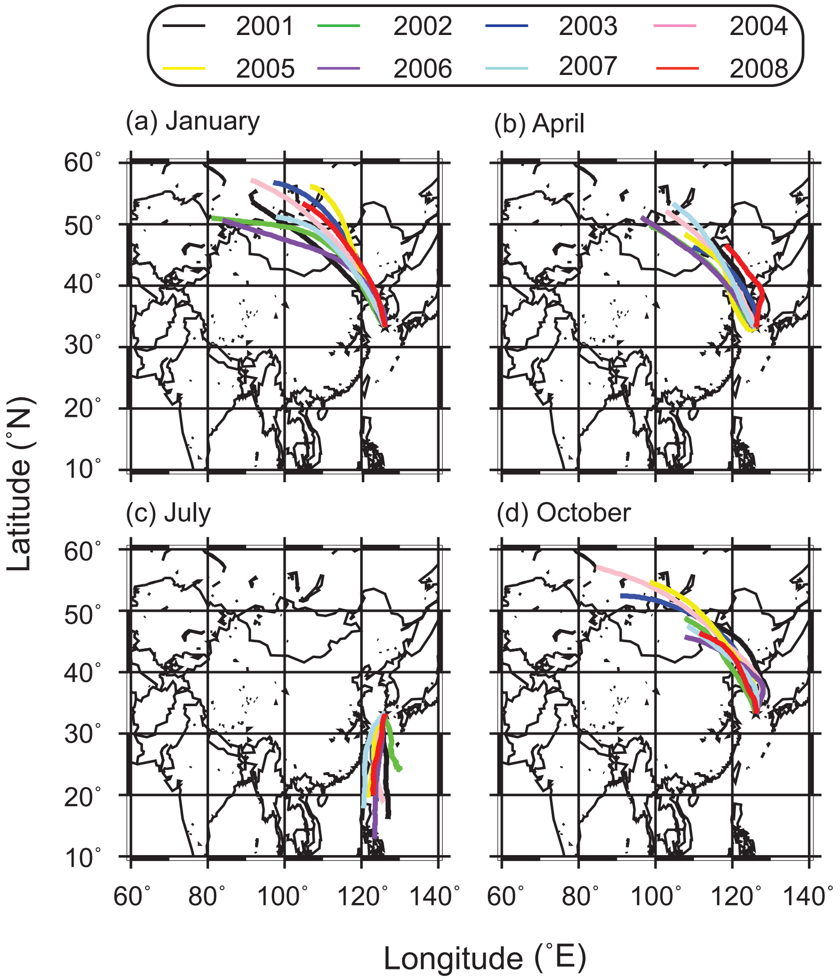
Fig. 7. Correlations of levoglucosan (a biomass burning tracer) with saturated (a - e) and unsaturated (f - h) diacids in aerosol samples collected from 2003 April to 2004 April. (a) oxalic (C_2), (b) azelaic (C_9), (c) methylsuccinic (iC_5), (d) ketopimelic (kC_7), (e) ketomalonic (kC_3), (f) maleic (M), (g) phthalic (Ph) and (h) terephthalic (tPh) acids. Note that data have been segregated by the season.

Fig. 8. Boxplots depicting the interannual (2001-2008) trends of major saturated (a - f) and unsaturated (g - h) diacids in April. (a) oxalic (C_2), (b) malonic (C_3), (c) succinic (C_4), (d) adipic (C_6), (e) azelaic acid (C_9), (f) methylsuccinic (iC_5), (g) isophthalic (iPh), and (h) phthalic (Ph) acids. The trends of interannual variations for the other months are shown in Table S1. The lower, middle, and upper lines in the box are related with the 25th, 50th and 75th percentiles, respectively. The lower and upper whiskers represent the 10th and 90th

percentiles, respectively. The r^2 values were calculated based on the median concentrations using a linear regression analysis.

Fig. 9. Boxplots depicting interannual (2001-2008) trends in April. (a) carbon monoxide (CO), (b) glyoxylic acid (ωC_2), (c) glyoxal (Gly), and (d) methylglyoxal (MGly). The trends of interannual variations for the other months are shown in Table S2. The lower, middle, and upper lines in the box are related with the 25th, 50th and 75th percentiles, respectively. The lower and upper whiskers represent the 10th and 90th percentiles, respectively. The r^2 values were calculated based on the median concentrations using a linear regression analysis.

Fig. 1.



2001
2002
2003
2004
2005
2006
2007
2008
(a) January
(b) April
(c) July
(d) October
60˚
50˚
40˚
30˚
20˚
10˚
Latitude (˚N)
60˚
80˚
100˚
120˚
140˚
Longitude (˚E)

Fig. 2.

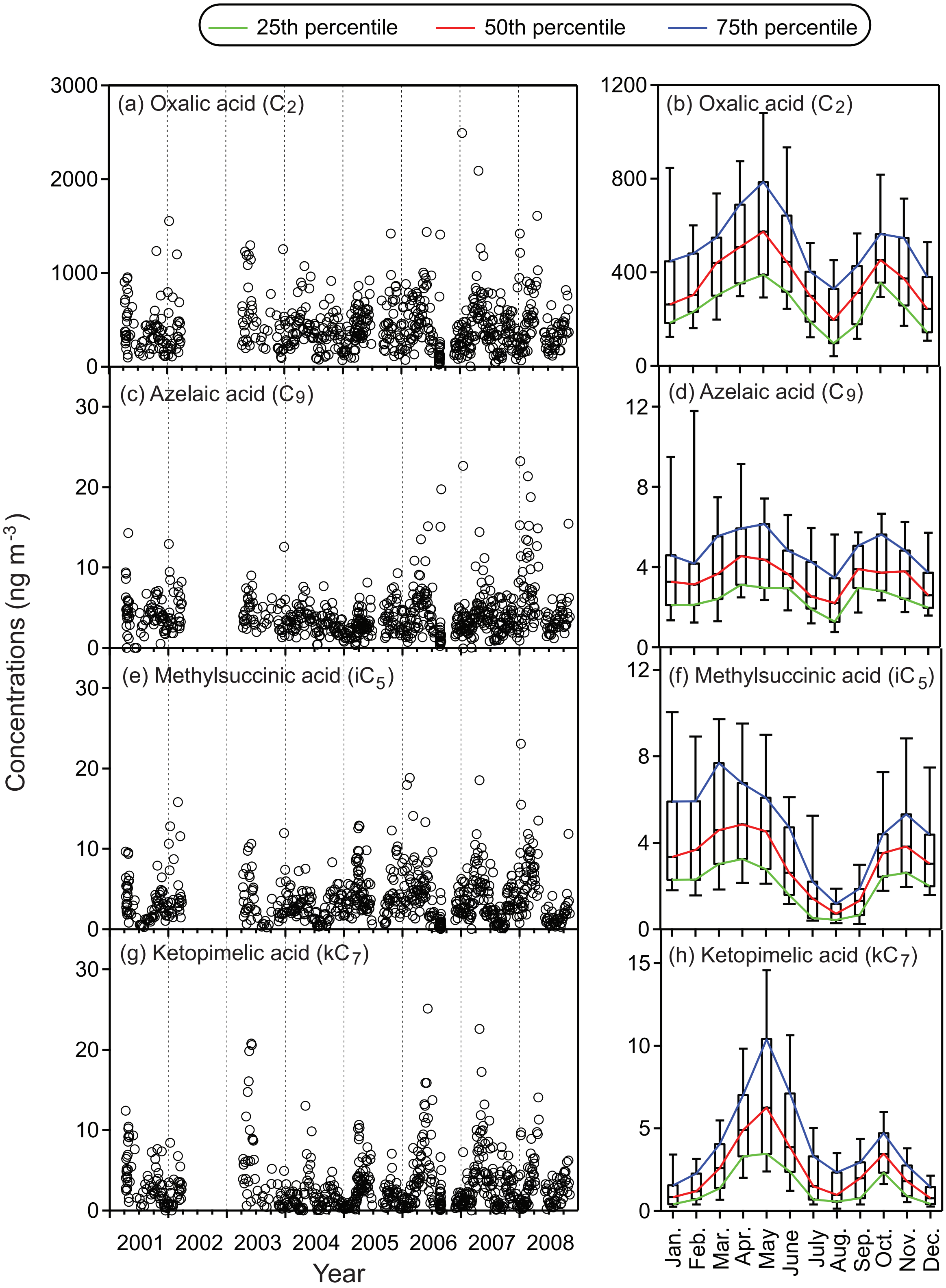

25th percentile
50th percentile
75th percentile
(a) Oxalic acid (C_2)
(b) Oxalic acid (C_2)
(c) Azelaic acid (C_9)
(d) Azelaic acid (C_9)
(e) Methylsuccinic acid (iC_5)
(f) Methylsuccinic acid (iC_5)
(g) Ketopimelic acid (kC_7)
(h) Ketopimelic acid (kC_7)
Concentrations (ng m^{-3})
0
1000
2000
3000
400
800
1200
10
20
30
4
8
12
5
15
2001
2002
2003
2004
2005
2006
2007
2008
Year
Jan.
Feb.
Mar.
Apr.
May
June
July
Aug.
Sep.
Oct.
Nov.
Dec.

Fig. 3.

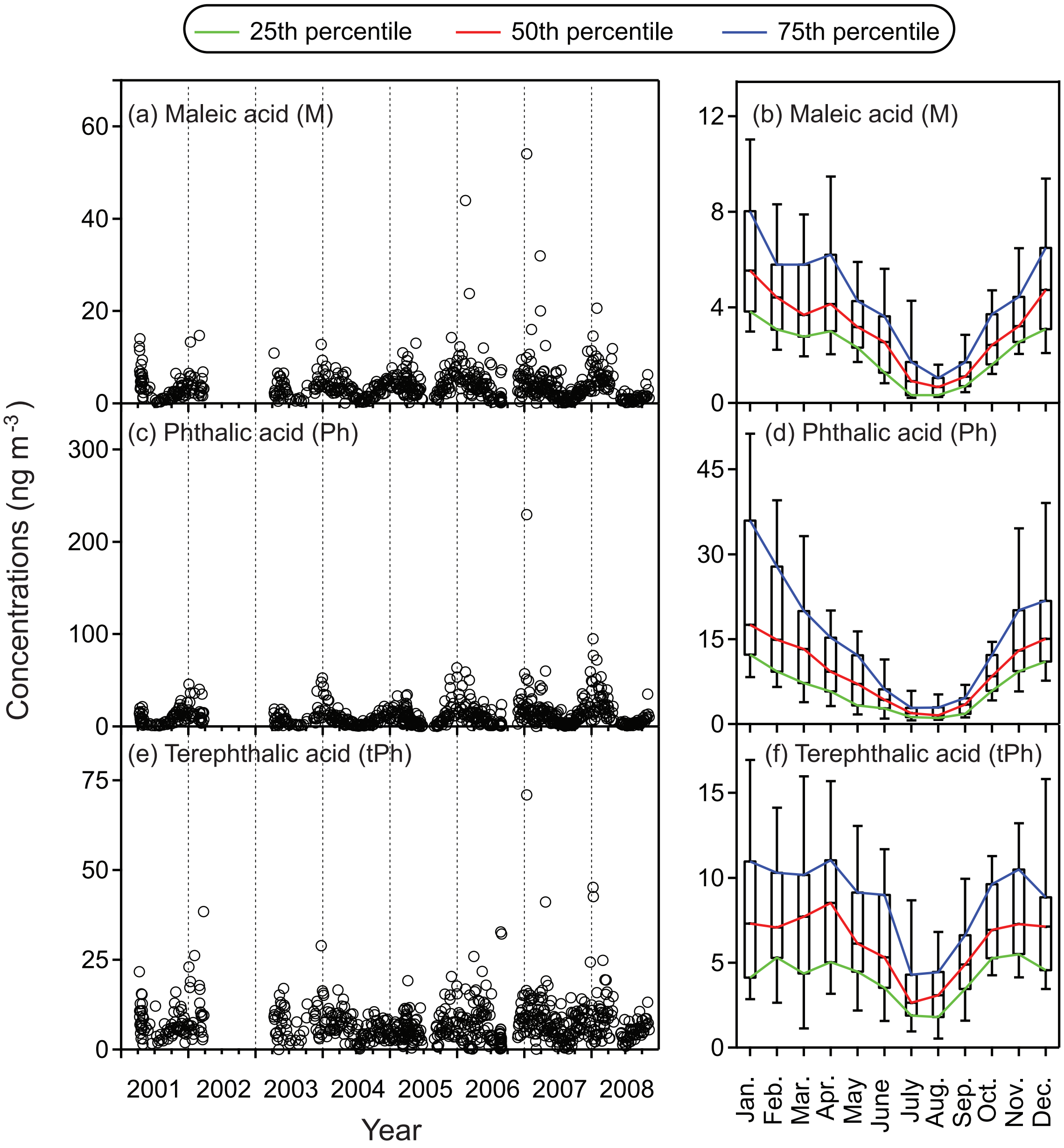

25th percentile
50th percentile
75th percentile
Concentrations (ng m^{-3})
(a) Maleic acid (M)
0
20
40
60
(b) Maleic acid (M)
0
4
8
12
(c) Phthalic acid (Ph)
0
100
200
300
(d) Phthalic acid (Ph)
0
15
30
45
(e) Terephthalic acid (tPh)
0
25
50
75
(f) Terephthalic acid (tPh)
0
5
10
15
2001
2002
2003
2004
2005
2006
2007
2008
Year
Jan.
Feb.
Mar.
Apr.
May
June
July
Aug.
Sep.
Oct.
Nov.
Dec.

Fig. 4.

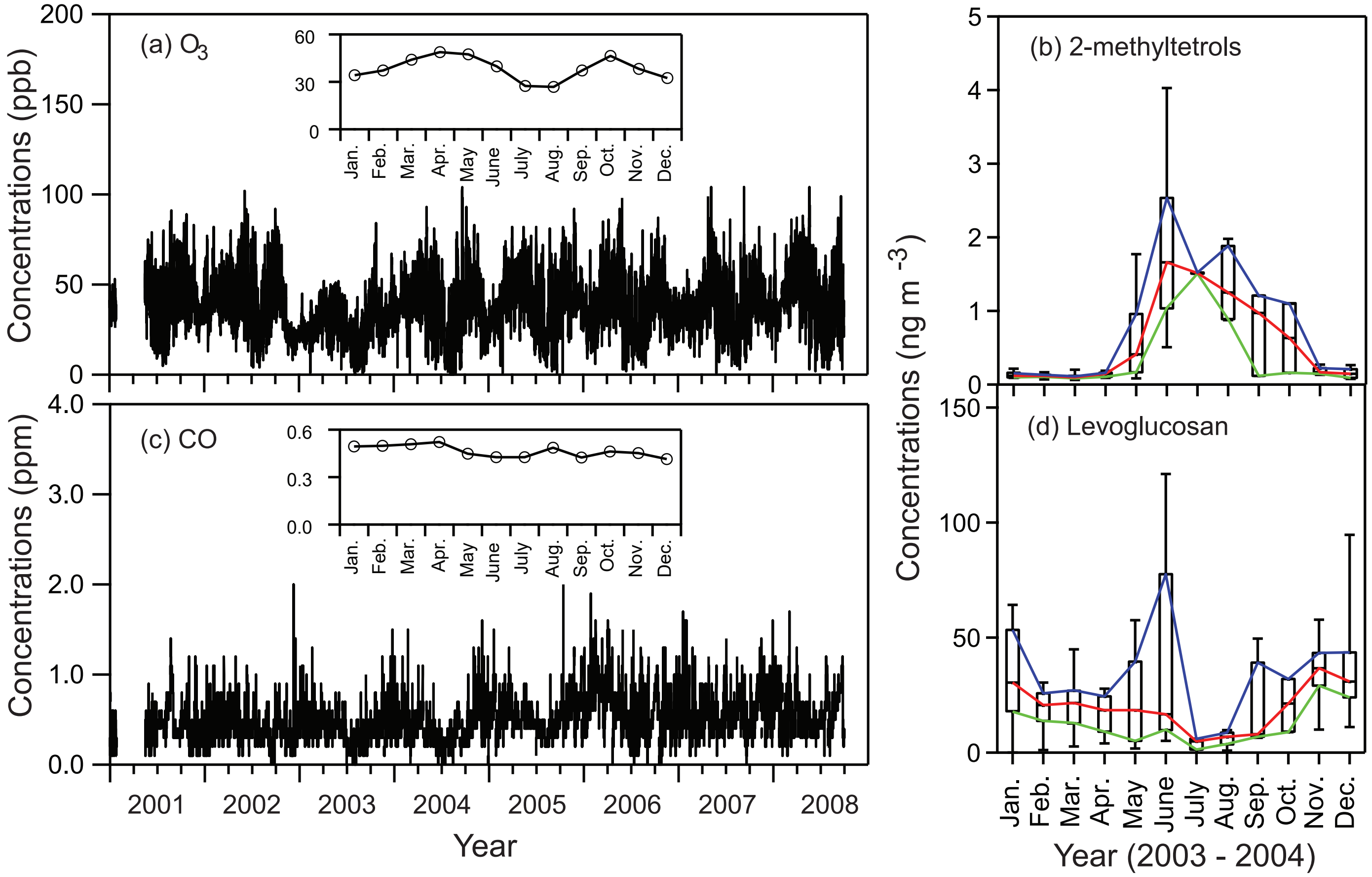
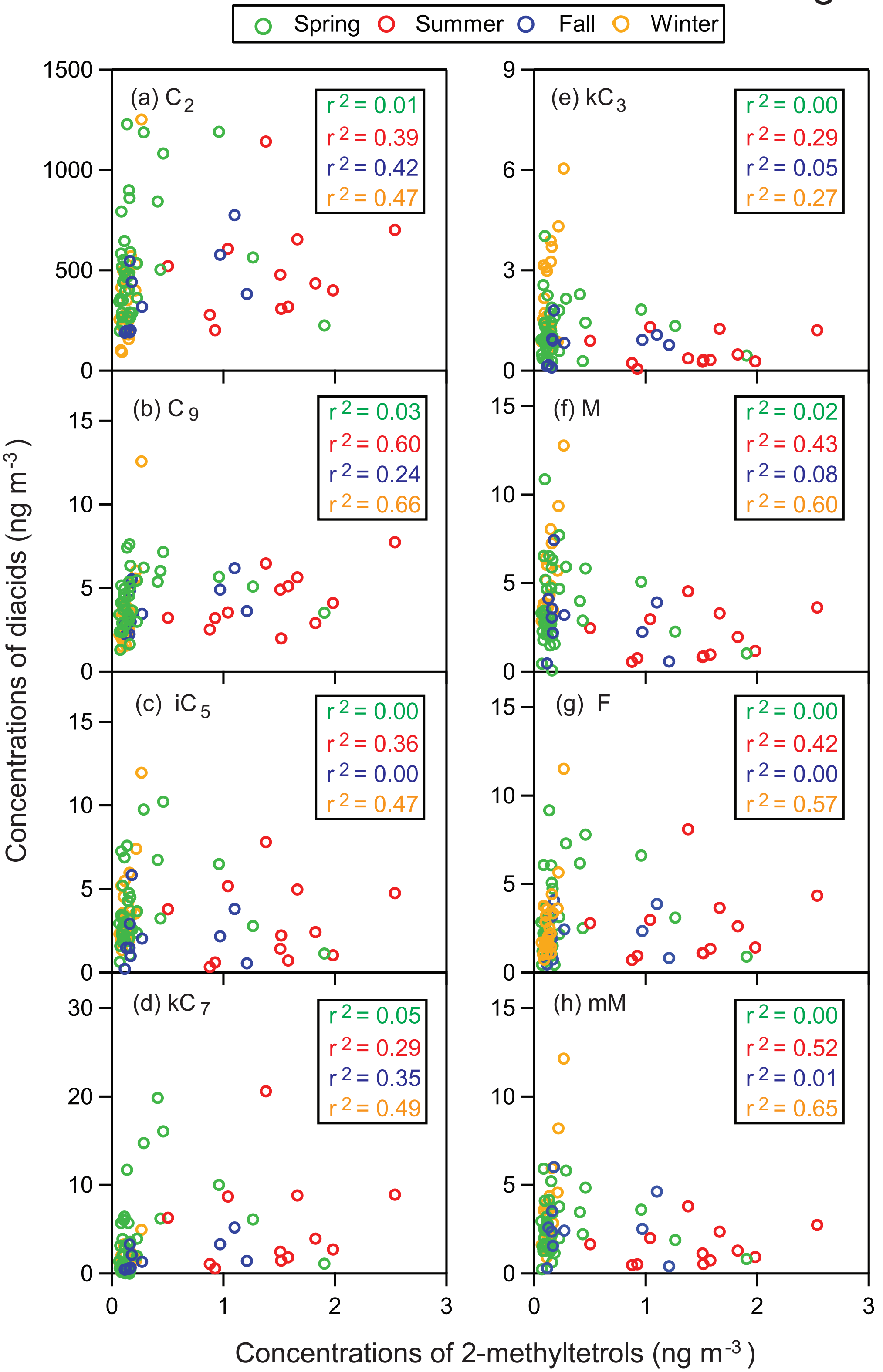

(a) O_3
Concentrations (ppb)
200
150
100
50
0
60
30
0
Jan.
Feb.
Mar.
Apr.
May
June
July
Aug.
Sep.
Oct.
Nov.
Dec.
(c) CO
Concentrations (ppm)
4.0
3.0
2.0
1.0
0.0
0.6
0.3
0.0
2001
2002
2003
2004
2005
2006
2007
2008
Year
(b) 2-methyltetrols
5
4
3
2
1
0
Concentrations (ng m $^{-3}$)
(d) Levoglucosan
150
100
50
0
Year (2003 - 2004)

Fig. 5.



○ Spring ○ Summer ○ Fall ○ Winter
(a) C2
r 2 = 0.01
r 2 = 0.39
r 2 = 0.42
r 2 = 0.47
(b) C 9
r 2 = 0.03
r 2 = 0.60
r 2 = 0.24
r 2 = 0.66
(c) iC 5
r 2 = 0.00
r 2 = 0.36
r 2 = 0.00
r 2 = 0.47
(d) kC 7
r 2 = 0.05
r 2 = 0.29
r 2 = 0.35
r 2 = 0.49
(e) kC3
r 2 = 0.00
r 2 = 0.29
r 2 = 0.05
r 2 = 0.27
(f) M
r 2 = 0.02
r 2 = 0.43
r 2 = 0.08
r 2 = 0.60
(g) F
r 2 = 0.00
r 2 = 0.42
r 2 = 0.00
r 2 = 0.57
(h) mM
r 2 = 0.00
r 2 = 0.52
r 2 = 0.01
r 2 = 0.65
1500
1000
500
0
9
6
3
15
10
5
30
20
0
1
2
3
Concentrations of diacids (ng m-3)
Concentrations of 2-methyltetrols (ng m-3)

Fig. 6.

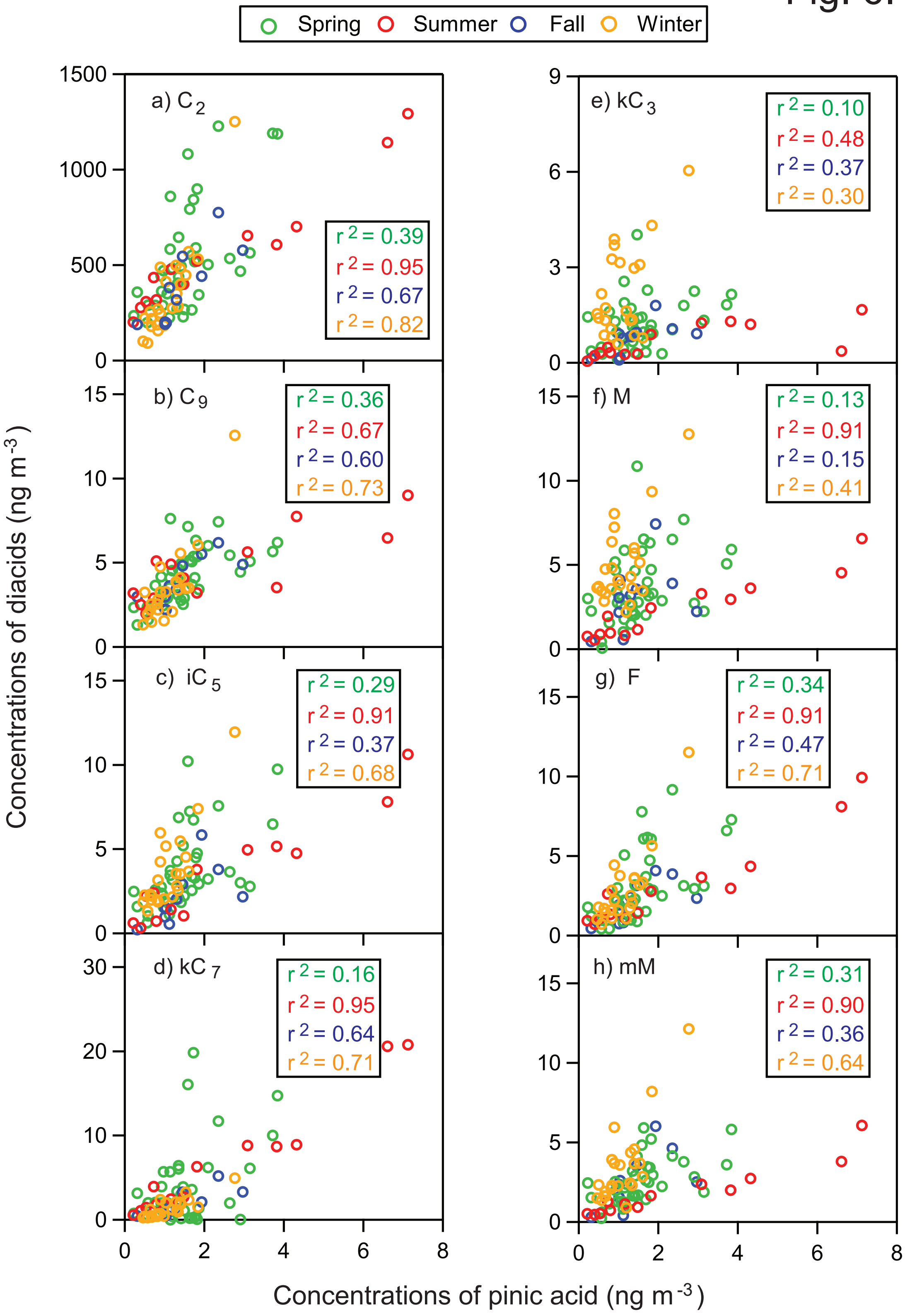
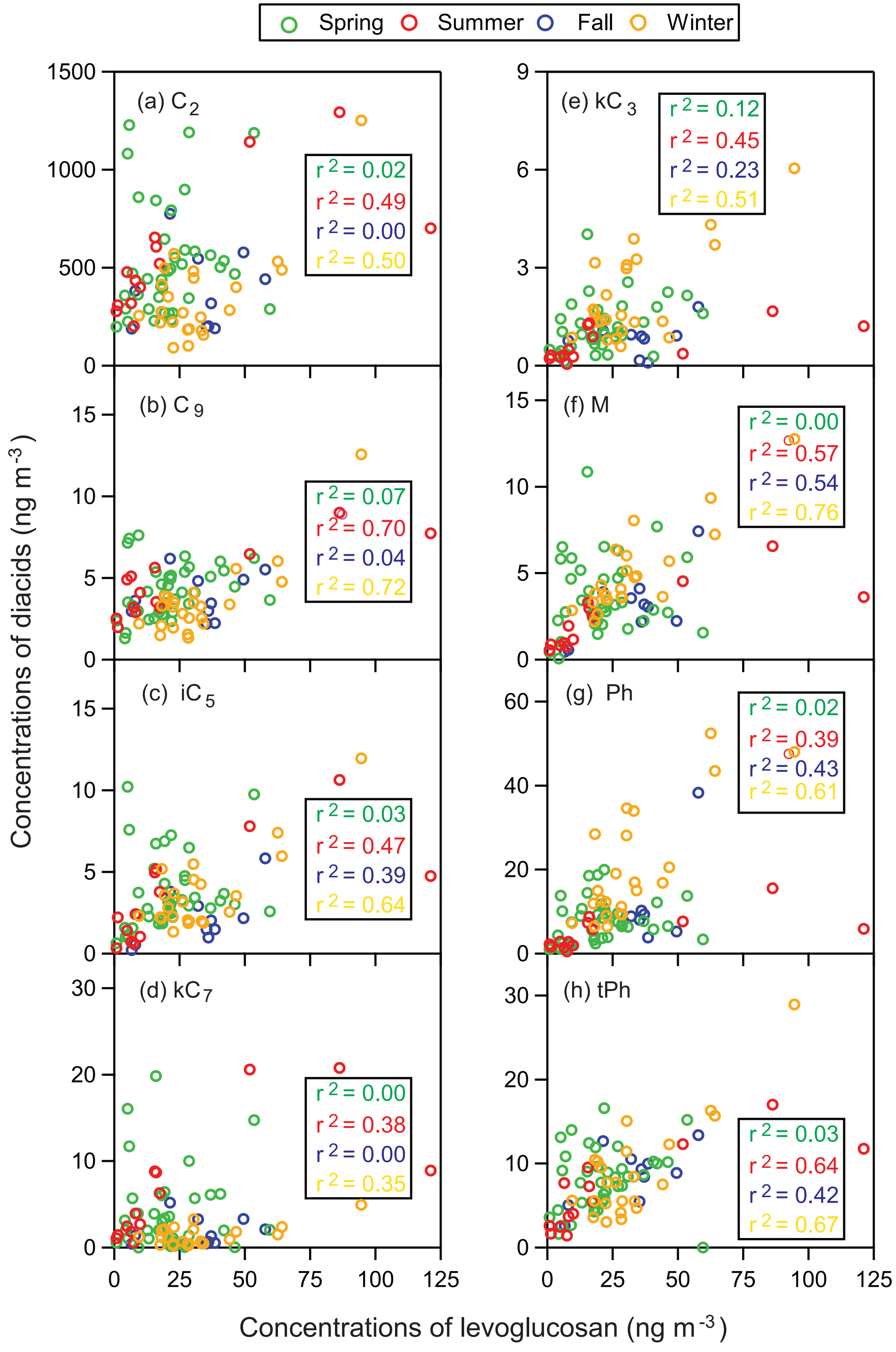

○ Spring ○ Summer ○ Fall ○ Winter
a) C_2
$r^2 = 0.39$
$r^2 = 0.95$
$r^2 = 0.67$
$r^2 = 0.82$
b) C_9
$r^2 = 0.36$
$r^2 = 0.67$
$r^2 = 0.60$
$r^2 = 0.73$
c) iC_5
$r^2 = 0.29$
$r^2 = 0.91$
$r^2 = 0.37$
$r^2 = 0.68$
d) kC_7
$r^2 = 0.16$
$r^2 = 0.95$
$r^2 = 0.64$
$r^2 = 0.71$
e) kC_3
$r^2 = 0.10$
$r^2 = 0.48$
$r^2 = 0.37$
$r^2 = 0.30$
f) M
$r^2 = 0.13$
$r^2 = 0.91$
$r^2 = 0.15$
$r^2 = 0.41$
g) F
$r^2 = 0.34$
$r^2 = 0.91$
$r^2 = 0.47$
$r^2 = 0.71$
h) mM
$r^2 = 0.31$
$r^2 = 0.90$
$r^2 = 0.36$
$r^2 = 0.64$
1500
1000
500
0
15
10
5
0
30
20
10
9
6
3
0
2
4
6
8
Concentrations of diacids (ng m^{-3})
Concentrations of pinic acid (ng m^{-3})

Fig. 7.



Spring
Summer
Fall
Winter
(a) C2
r² = 0.02
r² = 0.49
r² = 0.00
r² = 0.50
(b) C9
r² = 0.07
r² = 0.70
r² = 0.04
r² = 0.72
(c) iC5
r² = 0.03
r² = 0.47
r² = 0.39
r² = 0.64
(d) kC7
r² = 0.00
r² = 0.38
r² = 0.00
r² = 0.35
(e) kC3
r² = 0.12
r² = 0.45
r² = 0.23
r² = 0.51
(f) M
r² = 0.00
r² = 0.57
r² = 0.54
r² = 0.76
(g) Ph
r² = 0.02
r² = 0.39
r² = 0.43
r² = 0.61
(h) tPh
r² = 0.03
r² = 0.64
r² = 0.42
r² = 0.67
0
500
1000
1500
0
5
10
15
0
5
10
15
0
10
20
30
0
3
6
9
0
5
10
15
0
20
40
60
0
10
20
30
0
25
50
75
100
125
0
25
50
75
100
125
Concentrations of diacids (ng m-3)
Concentrations of levoglucosan (ng m-3)

Fig. 8.

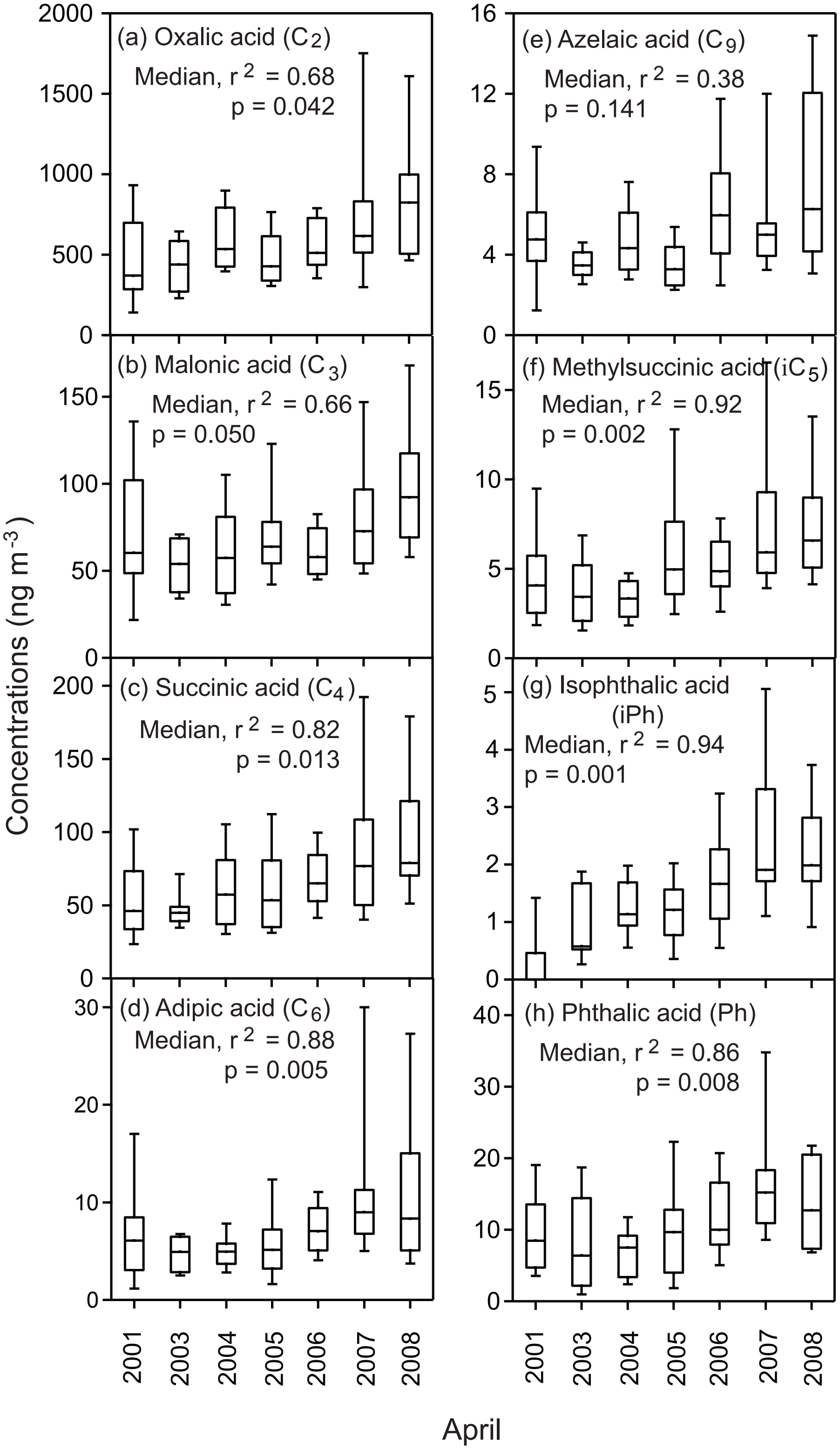
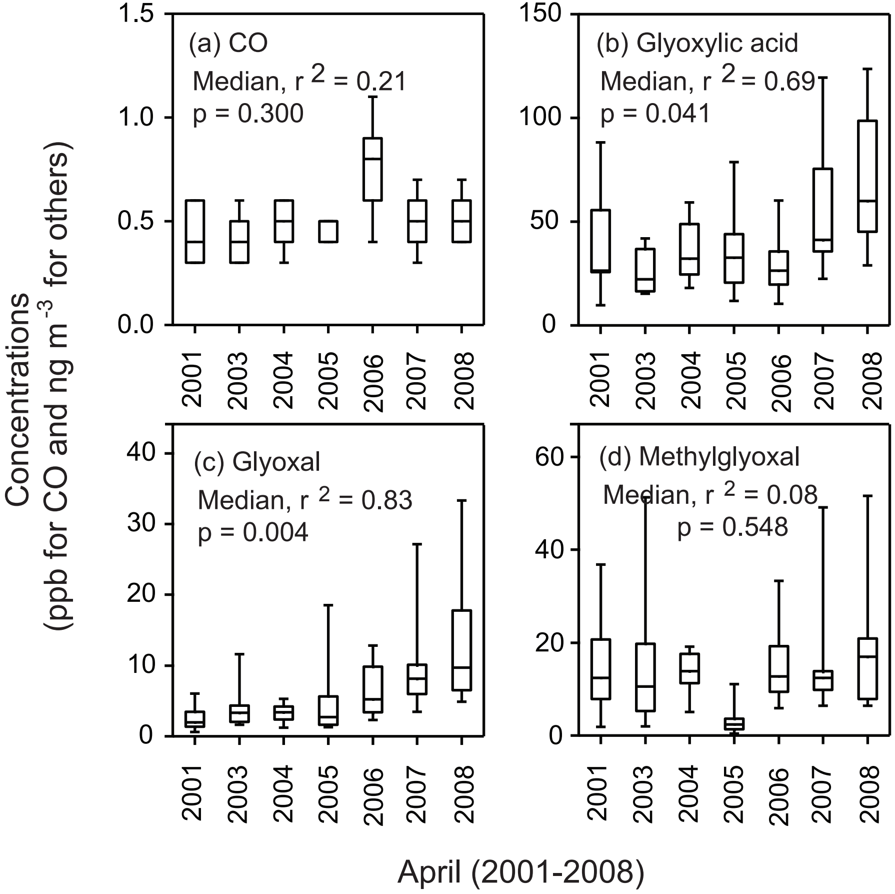

(a) Oxalic acid (C2)
Median, r 2 = 0.68
p = 0.042
2000
1500
1000
500
0
(b) Malonic acid (C 3)
Median, r 2 = 0.66
p = 0.050
150
100
50
0
(c) Succinic acid (C4)
Median, r 2 = 0.82
p = 0.013
200
150
100
50
0
(d) Adipic acid (C6)
Median, r 2 = 0.88
p = 0.005
30
20
10
0
(e) Azelaic acid (C9)
Median, r 2 = 0.38
p = 0.141
16
12
8
4
0
(f) Methylsuccinic acid (iC5)
Median, r 2 = 0.92
p = 0.002
15
10
5
0
(g) Isophthalic acid
(iPh)
Median, r 2 = 0.94
p = 0.001
5
4
3
2
1
0
(h) Phthalic acid (Ph)
Median, r 2 = 0.86
p = 0.008
40
30
20
10
0
Concentrations (ng m-3)
2001
2003
2004
2005
2006
2007
2008
April

Fig. 9.



(a) CO
Median, r^2 = 0.21
p = 0.300
(b) Glyoxylic acid
Median, r^2 = 0.69
p = 0.041
(c) Glyoxal
Median, r^2 = 0.83
p = 0.004
(d) Methylglyoxal
Median, r^2 = 0.08
p = 0.548
Concentrations
(ppb for CO and ng m^{-3} for others)
April (2001-2008)
2001
2003
2004
2005
2006
2007
2008
0.0
0.5
1.0
1.5
0
50
100
150
0
10
20
30
40
0
20
40
60