Enhanced concentrations of citric acid in spring aerosols collected at Gosan background site in East Asia

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Abstract

Elevated concentrations of atmospheric citric acid (range: 20−320 ng m^{-3}) were observed in total suspended particles collected at Gosan background site in Jeju Island, Korea during mid- to late April of 2007 and 2008. In order to specify the sources of citric acid, water-soluble dicarboxylic acids and related compounds were measured in the pollen sample collected at the Gosan site (Pollen_Gosan), authentic pollen samples from Japanese cedar (Pollen_cedar) and Japanese cypress trees (Pollen_cypress), and tangerine fruit produced from Jeju Island. Citric acid (2790 ng in unit mg of pollen mass) was found as most abundant species in the Pollen_Gosan, followed by oxalic acid (2390 ng mg^{-1}). Although citric acid was not detected in the Pollen_cedar and Pollen_cypress as major species, it was detected in the tangerine juice as a dominant species while malic acid was detected as major species in the tangerine peel, followed by oxalic and citric acids. Since Japanese cedar trees are planted around tangerine farms to prevent strong winds from the Pacific Ocean, citric acid that may be directly emitted from tangerine is likely adsorbed on pollens emitted from Japanese cedar and then transported to the Gosan site. Much lower malic/citric acid ratios under cloudy condition than clear condition suggest that malic acid may rapidly decompose to lower molecular weight compounds such as oxalic and malonic acids (<C4) via aqueous phase reaction in cloud during the atmospheric transport.

1 Introduction

Jeju Island, Korea is located at the boundary of the Yellow Sea and the East China Sea and surrounded by mainland China, Korean Peninsular, and Kyushu Island, Japan. Gosan site is located on the western edge of Jeju Island facing the Asian continent and is isolated from residential areas of the island (Kawamura et al., 2004). In order to understand physicochemical and radiative properties of anthropogenic aerosols under Asian continental outflow, several international experiments have been conducted at the Gosan site such as ACE-Asia (Aerosol Characterization Experiment–Asia) (Huebert et al., 2003) and ABC-EAREX 2005 (Atmospheric Brown Cloud–East Asia Regional Experiment 2005) (Nakajima et al., 2007). To better understand chemical and physical properties of aerosols mainly transported from Asian continent, contributions of local effects on the Gosan site aerosols should be qualitatively and quantitatively evaluated.

Pollen is one of the important sources of bioaerosols (Solomon, 2002). They can cause serious allergic problems to human health (Solomon, 2002) and visibility impairment (Kim, 2007). Most pollen blowing events occur during the growing season of plants from March to May in Korea (Oh et al., 1998). Pollen emission from plants is controlled by air temperature, relative humidity, and wind speed (Doskey and Ugoagwu, 1989; Puc and Wolski, 2002; Palacios et al., 2007). Since airborne pollen can be transported very long distance (Porsbjerg et al., 2003; Rousseau et al., 2008), airborne pollen is not only local problem but also regional and intercontinental problems. The pollens from local plants in Jeju Island can cause an increase of organic aerosol mass and may overestimate relevant radiative forcing by *in situ* observations compared to a prediction by chemical transport model (Huebert et al., 2003). However, there were no studies regarding the impact of the pollens on the aerosol chemical composition at the

Gosan site.

Malic and citric acids are present in atmospheric particles (Kawamura and Ikushima, 1993; Fu et al., 2008). They are highly water soluble and, thus, their distinct hygroscopic growths have been observed as a function of water saturation ratio (Yalkowsky, 1989; Verschueren, 1996; Joutsensaari et al., 2001). Malic acid can be secondarily produced from succinic acid through aqueous phase photo-oxidation in cloud (Altieri et al., 2008). However, it was also found in grape juice and food products (e.g., Canadian maple sugar) (Cowles, 1908; Schenker and Rieman, 1953). Citric acid predominantly exits in lemon and other citrus juice (Schenker and Rieman, 1953). However, source and decomposition pathway of malic and citric acids in aerosols are still not well understood.

In the course of the study on total suspended particles (TSP) collected at the Gosan site for dicarboxylic acids and related compounds, we discovered high abundances of citric and malic acids in spring. Here, we report the temporal variations of these hydroxy acids in the aerosols as well as pollens and tangerine fruit, and discuss the sources and transport mechanisms of citric acid and airborne pollen. Photochemical production and degradation of malic acid during the transport is also discussed.

2 Measurements

Sampling of TSP was carried out at Gosan site (33.17°N; 126.10°E) in Jeju Island, over 2−5 days integration during 23 March to 1 June 2007 and 16−24 April 2008. TSP samples were collected on pre-combusted quartz fiber filters (20 x 25 cm) using a high volume air sampler (Kimoto AS-810) installed on the rooftop of a trailer (~3 m above the ground). Before and after the filter sampling, the samples were stored in clean glass

jars (150 mL) with Teflon-lined screw cap at -20 °C prior to analysis. Field blank filters were collected every month. Hourly ambient temperature and cloud cover data were obtained from the Korean meteorological administration at the Gosan observatory. The value of cloud cover ranges from 0 (no cloud) to 10 (completely cloudy).

2.1 Atmospheric aerosol samples and authentic pollen and tangerine

Pollen events were observed at the Gosan site during mid- to late April of 2007 and 2008. Identification of pollen events are conducted based on daily human observation and the microscope image of pollens collected in TSP samples. Total 8 pollen-enriched TSP samples were collected in 2007 (11−23 April of 2007) and 2008 (16−24 April of 2008) over 2−5 days integration. Specifications of sampling, ambient temperature, and cloud cover at the Gosan site during the pollen episodes in 2007 and 2008 were summarized in Table 1.

Three types of pollen samples were analyzed for water-soluble dicarboxylic acids and related compounds. Two standard pollen samples from Japanese cedar (Pollen_cedar) and Japanese cypress (Pollen_cypress) were obtained from the WAKO Chemical Co. (product No. 168-20911 for Japanese cedar and 165-20921 for Japanese cypress). Additionally, airborne pollens (Pollen_Gosan), which were mainly originated from Japanese cedar trees nearby tangerine farms in Jeju Island, were separated from an aliquot of the TSP filter sample (KOS751) collected during the severe pollen episode (16−21 April 2008) by mild vibration. Tangerine fruit produced from Jeju Island was also prepared.

2.2 Chemical analysis

An aliquot (11.34 cm^2) of filter sample was extracted with ultra pure organic-free Milli-Q water (10 mL x 3 times) and dicarboxylic acids and related compounds were analyzed using a capillary gas chromatograph (GC) (Hewlett-Packard, HP6890) equipped with a flame ionization detector by a method of Kawamura and Ikushima (1993). GC/mass spectrometry was used for the peak identification. Recoveries of authentic standards spiked to a pre-combusted quartz fiber filter were 85% for oxalic acid and more than 90% for malonic, succinic, glutaric, and adipic acids. The analytical errors of major species were less than 5% based on the triplicate analyses of different sections of the same filter sample. Concentrations of all the species reported here are corrected for the field blanks but not for recoveries.

0.87 mg of the Gosan pollen and ~2 mg of the standard Pollen_cedar and Pollen_cypress were weighed using a microbalance (Satorius, M2P) and extracted with the Milli-Q water (10 mL x 3 times). Aliquots of the tangerine inner part and peel (outer cover) were extracted with the Milli-Q water (10 mL x 3 times). In order to prevent possible contamination over the surface of tangerine fruit, tangerine surface was mildly washed with the Milli-Q water three times. The water extracts of authentic standard pollen samples and tangerine fruit are analyzed for dicarboxylic acids and related compounds using the same technique used for the TSP sample analyses.

3 Results and discussion

3.1 Temporal variations of citric, malic, succinic, and oxalic acids in the pollen-enriched TSP samples

3.1.1 Springtime pollen episode in Gosan background site

Tangerine is an orange-colored citrus fruit which is the most popular farm product

in Jeju Island. Most tangerines consumed in South Korea are cultivated in Jeju Island with an annual production of 739,000 tons in 2009 (Annual statistics in Jeju special self-governing province, 2009). The cultivating area of tangerine in Jeju Island is ~209 km^2, which accounts for ~11% of the total area of Jeju Island. There are two harvesting season of tangerine fruits; i.e., late fall (November~) for a natural cultivation and mid-spring (April~) for a green house cultivation.

In order to prevent strong winds from the Pacific Ocean, all tangerine farms are surrounded by Japanese cedar trees. Pollen blowing in Jeju Island in April was mainly originated from the Japanese cedar trees (Agricultural research institute in Jeju special self-governing province, personal communication). Thus, it was postulated that the airborne pollens at the Gosan site in April might be affected by biogenic emissions from tangerine fruits.

3.1.2 Unique distributions of citric and malic acids in the pollen-enriched TSP samples

Temporal variations of citric, malic, succinic (C_4), and oxalic (C_2) acids are shown in Fig. 2, together with average cloud cover. Citric acid showed unique temporal pattern with elevated concentrations during mid- to late April of 2007 and 2008, which have not been reported previously. Increases of citric acid coincided well with the pollen episodes in 2007 and 2008 marked in Fig. 2. Concentrations of citric acid ranged from 20 ng m^{-3} to 320 ng m^{-3} during the pollen episodes of 2007 and 2008 with an average of 120 ± 120 ng m^{-3}, whereas low concentrations of citric acid were observed during the non-pollen episodes (range: 0.2−18 ng m^{-3}, avg.: 3.7 ± 4.6 ng m^{-3}). However, no enhanced concentrations of C_2 and C_4 were observed during the pollen episodes

compared to the non-pollen episodes. Overall temporal pattern of malic acid was generally well correlated with those of citric acid with elevated concentrations during the pollen episodes. However, concentrations of malic acid didn't increase during the cloudy period of the pollen episodes, being different from citric acid. The temporal pattern of malic acid will be discussed in detail with respect to cloud cover in section 3.3.

Histograms of dicarboxylic acids and related compounds during the severe pollen episodes (KOS751 and KOS752) are shown in Fig. 3. Concentrations of the total detected organic acids during the severe pollen episodes were 1800 ± 150 ng m^{-3}. C_2 was found as the most abundant species, which accounts for 49% of the total detected organic acids, followed by citric acid (avg. 17%). The level of citric acid reached one-third of C_2. Similar amounts of C_3, C_4, and glyoxylic (ωC_2) acids were detected as major species (avg. 5.4%−6.0%). Additionally, high concentrations of malic acid were detected (avg. 3.5%).

Relatively low concentrations of adipic (C_6) and phthalic (Ph) acids were detected (avg. 0.7 % for C_6 and 0.6% for Ph). Since C_6 and Ph may be produced by the oxidation of anthropogenic cyclohexene (Grosjean et al., 1978; Hatakeyama et al., 1987) and aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993), respectively, relatively low concentrations of C_6 and Ph indicates that direct emissions from anthropogenic sources were insignificant during the severe pollen episodes. Rather, abundances of near end products (C_2, C_3, C_4, and ωC_2) suggest that aged air masses were dominant during the severe pollen episodes.

3.2 Molecular distribution of water-soluble dicarboxylic acids and related compounds

in airborne pollen and tangerine fruit

3.2.1 Airborne pollens from Japanese cedar and Japanese cypress

Total concentrations of water-soluble dicarboxylic acids and related compounds detected in the standard Pollen_cedar and Pollen_cypress were 751 and 749 ng mg^{-3} (ng of a compound in mg of pollen mass), respectively (Table 2). C_2 was found as the most abundant species, which accounts for 68% and 60% of the total detected organic acids for the Pollen_cedar and Pollen_cypress, respectively. Small peaks of low molecular weight species such as C_3, C_4, ωC_2, and pyruvic acid (Pyr) were detected, which are near end products of multiphase organic chemistry (Ervens et al., 2004; Legrand et al., 2007). This suggests that the atmospheric organic acids can be adsorbed on pollen during transport and transported together.

The Pollen_Gosan showed similar molecular distribution of dicarboxylic acids and related compounds with elevated concentration of C_2 (~33% of the total detected organic acids), followed by C_4, C_3, and ωC_2, implying that these organic acids might be adsorbed on the surface of the Pollen_Gosan during the transport. The adsorption may also be occurred during filter sampling. Surprisingly, in addition to the abundances of the near end products, citric acid was found as the most abundant species (~38%). Predominance of citric acid in airborne pollen has not been reported previously.

3.2.2 Tangerine juice and peel

The mass ratios of each compound relative to citric acid in the tangerine juice and peel are shown in Fig. 4. Citric acid was detected as the most abundant species in the tangerine juice which was ~50 times higher than the second dominant species (malic acid). C_2, C_3, and C_4 were detected with the mass ratios relative to citric acid

(0.0065−0.0075). The tangerine peel showed a predominance of malic acid, followed by C_2, citric acid, and C_3. Less abundant C_4, Pyr, ωC_2, mGly, and glyoxal (Gly) were also detected. Even though the tangerine peel showed the similar distribution with the tangerine juice, their magnitudes were quite different. Malic acid was detected as the most abundant species in the tangerine peel, which is ~2.3 times higher than citric acid. C_2 and C_3 were also comparable with citric acid. The predominance of malic acid and comparable abundances of C_2, C_3 and citric acid are unique in the tangerine peel.

3.3 Sources and photochemical degradation of citric and malic acids in the atmosphere

Citric acid was found as the dominant species in the Pollen_Gosan while it existed at negligible level in the standard Pollen_cedar and Pollen_cypress. High concentrations of citric and malic acids were detected in the tangerine juice and peel as well as the TSP samples collected during the pollen episodes. Since tangerine farms are surrounded by Japanese cedar trees to prevent strong winds from the Pacific Ocean, citric and malic acids that are directly emitted from tangerine fruits are likely adsorbed on airborne pollens emitted from Japanese cedar and transported to the Gosan site. A strong positive correlation (R^2 = 0.81) was found between malic and citric acids, supporting similar source of malic and citric acids.

Figure 5 shows scatter plot of malic acid versus citric acid concentrations in the TSP samples during the pollen episodes and tangerine peel with respect to average cloud cover. Mass ratios of malic acid to citric acid during the pollen episodes ranged 0.01 to 0.61 with an average of 0.23. Interestingly, the mass ratios of aerosol samples are higher during the relatively clear condition (average cloud cover ≤3). The mass ratios approached to that of the tangerine peel (2.3) as average cloud cover decreases (Fig. 5).

Much lower mass ratios of malic acid to citric acid under the cloudy condition (average cloud cover ≥6) than clear condition suggests that malic acid, which may be directly emitted from tangerine fruits, may rapidly decompose to smaller species via aqueous reaction in cloud during the transport (Yu et al., 2005). Positive correlation (R^2 = 0.78) was observed between the mass ratios of malic acid to citric acid and ambient temperature under the cloudy condition (average cloud cover ≥6) during the pollen episodes in 2007 (Fig. 6). Positive correlation was also observed under the clear condition. These results suggest that the emission of malic acid from tangerine peel is more enhanced than citric acid when ambient temperature increases.

A strong negative correlation (R^2 = 0.79) was observed between the mass ratios of malic acid to succinic acid and average cloud cover during the pollen episodes in 2007 (Fig. 7). This result suggests that malic acid might be secondarily produced by hydroxylation of succinic acid under strong solar radiation via photochemical processing (Kawamura and Ikushima, 1993). Thus, enhanced concentrations of malic acid during the pollen episodes may also be attributed to secondary production in the atmosphere.

4 Conclusion

High concentrations of citric acid were detected in the spring aerosols in East Asia as well as tangerine juice and peel, suggesting that these hydroxy acids can be directly emitted from tangerine fruits to the atmosphere. Since this compound is highly water-soluble and can alter the bulk hygroscopicity of aerosol particles (Abdul-Razzak and Ghan, 2004), emissions of citric acid from biogenic sources need further studies. High concentrations of airborne pollens were observed in the TSP samples collected at the

Gosan site during the pollen episodes in spring. These local pollens can cause an enhanced organic aerosol mass and may overestimate the relevant radiative forcing at the Gosan site. Thus, more studies are needed on organic aerosols in relation to chemical and optical properties of long-range transported pollutants around Asian continent during spring.

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Table 1. Specification of sampling, ambient temperature, and cloud cover at the Gosan site during the pollen episodes in 2007 and 2008.

Sample ID	Period*	Sample volume (m^3)	Ambient temperature	Cloud cover
KOS608	11−13 April 2007	2506	15 ± 2	3
KOS609	13−16 April 2007	3854	12 ± 1	7
KOS610	16−18 April 2007	2568	11 ± 1	8
KOS611	18−20 April 2007	2604	13 ± 2	3
KOS612	20−23 April 2007	3758	16 ± 2	9
KOS613	23−25 April 2007	2557	14 ± 2	6
KOS751	16−21 April 2008	5782	15 ± 2	6
KOS752	21−24 April 2008	3447	15 ± 3	8

*Quartz filter was changed between 10 A.M. and 11 A.M.

Table 2. Concentrations of dicarboxylic acids, tricarboxylic acid, ketocarboxylic acids, and α-dicarbonyls in the pollen samples from Japanese cedar and Japanese cypress.

Name of Compounds	Japanese Cedar (Gosan)*	Japanese Cedar (standard)	Japanese Cypress (standard)
Saturated n-dicarboxylic acids		(ng mg^{-1})**	
Oxalic, C_2	2390	507	449
Malonic, C_3	394	16	12
Succinic, C_4	588	33	83
Glutaric, C_5	95	3.1	4.2
Adipic, C_6	24	1.1	2.1
Pimelic, C_7	4.4	BDL***	BDL
Azelaic, C_9	124	2.8	23
Sebacic, C_{10}	BDL	12	BDL
Undecanedioic, C_{11}	BDL	BDL	BDL
Dodecanedioic, C_{12}	BDL	BDL	BDL
Branched dicarboxylic acids			
Methylmalonic, iC_4	11	BDL	18
Methylsuccinic, iC_5	BDL	BDL	BDL
Methylglutaric, iC_6	BDL	BDL	BDL
Unsaturated dicarboxylic acids			
Maleic, M	22	4.1	3.8
Fumaric, F	24	10	8.2
Methylmaleic, mM	10	BDL	BDL
Phthalic, Ph	70	9.3	4.9
Iso-phthalic, iPh	8	BDL	BDL
Tere-phthalic, tPh	14	BDL	BDL
Multifunctional dicarboxylic acids			
Malic, hC_4	40	BDL	BDL
Ketomalonic, kC_3	19	BDL	BDL
4-Ketopimelic, kC_7	19	BDL	BDL
Total dicarboxylic acids	**3857**	**598**	**609**
Saturated tricarboxylic acid			
Citric acid	2790	2.8	BDL
Ketocarboxylic acids			
Pyruvic, Pyr	83	34	38
Glyoxylic, ωC_2	306	59	48
3-Oxopropanoic, ωC_3	48	4.1	4.4
4-Oxobutanoic, ωC_4	75	19	15
5-Oxopentanoic, ωC_5	7.8	5.8	9.1
7-Oxoheptanoic, ωC_7	52	2.0	1.3
8-Oxooctanoic, ωC_8	50	BDL	1.2
9-Oxononanoic, ωC_9	6.9	7.1	5.6
Subtotal	**629**	**131**	**123**
α-Dicarbonyls			
Glyoxal, Gly	17	2.8	4
Methylglyoxal, mGly	45	17	13
Subtotal	**62**	**20**	**17**
Total (All detected species)	**7340**	**751**	**749**

*Japanese Cedar (Gosan) means pollen sample separated from TSP sample (KOS751, 16−21 April 2008). It should have adsorbed various organic components in the atmosphere.

**Mass concentrations of the detected compounds in total pollen mass.

***BDL: Below detection limit.

Figure captions

Figure 1. Map of the sampling site (33.17 °N, 126.10 °E) at Gosan in Jeju Island, located approximately 100 km south of the Korean peninsula

Figure 2. Temporal variations of citric, malic, succinic, and oxalic acids in the total suspended particle (TSP) samples collected at Gosan site during 23 March to 1 June of 2007 and 16−24 April 2008. Average cloud cover during each sampling period is also shown. The value of cloud cover ranges 0 (no cloud) to 10 (completely cloudy). Pollen 07 and Pollen 08 marked as red rectangular are during 11−25 April 2007 and 16−24 April 2008, respectively.

Figure 3. Average molecular distributions of dicarboxylic acids (diacids), ketocarboxylic acids (ketoacids), α-dicarbonyls, and tricarboxylic acid (triacid) in the TSP samples collected at the Gosan site during the severe pollen episodes (KOS751 and KOS752). To highlight the less abundant species, their molecular distributions are also shown with an enhanced y-axis scale. See Table 2 for abbreviations. KOS751 and KOS752 samples were collected during 16−21 April 2008 and 21-24 April 2008, respectively.

Figure 4. The mass ratios of each compound to citric acid detected in the (a) tangerine juice and (b) tangerine peel. See Table 2 for abbreviations.

Figure 5. Scatter plot of malic acid versus citric acid concentrations in the TSP samples during the pollen episodes and tangerine peel with respect to average cloud cover.

Figure 6. The mass ratios of malic acid to citric acid as a function of average ambient temperature during the pollen episodes in 2007. Clear and cloudy conditions represent average cloud cover <3 and >6, respectively.

Figure 7. The mass ratios of malic acid to succinic acid as a function of average cloud cover during the pollen episodes in 2007.

Figure 1

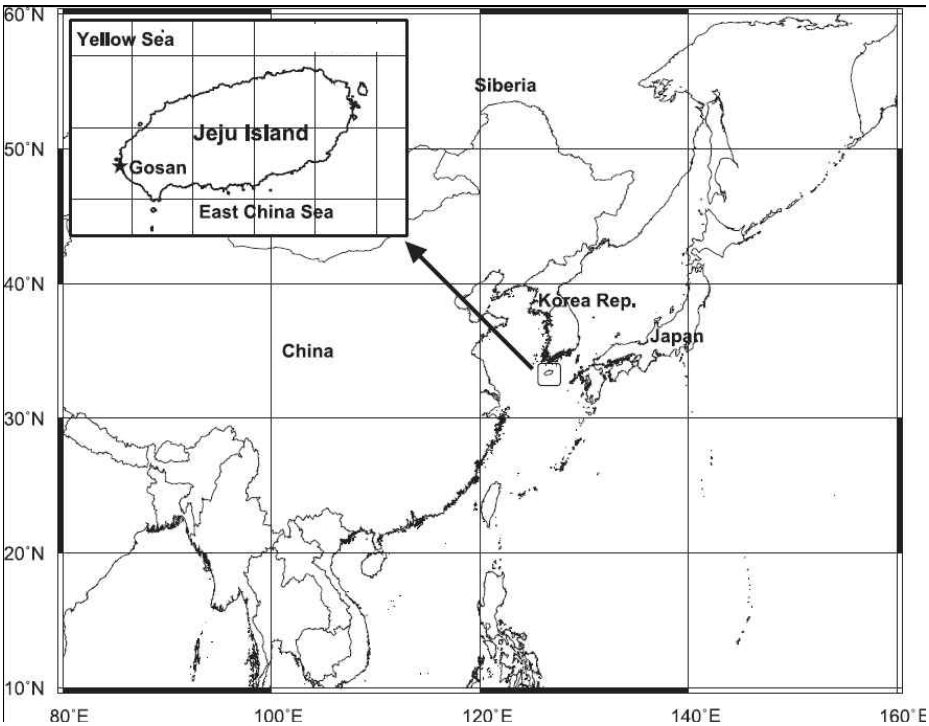

Yellow Sea
Jeju Island
Gosan
East China Sea
Siberia
Korea Rep.
Japan
China
60°N
50°N
40°N
30°N
20°N
10°N
80°E
100°E
120°E
140°E
160°E

Figure 2

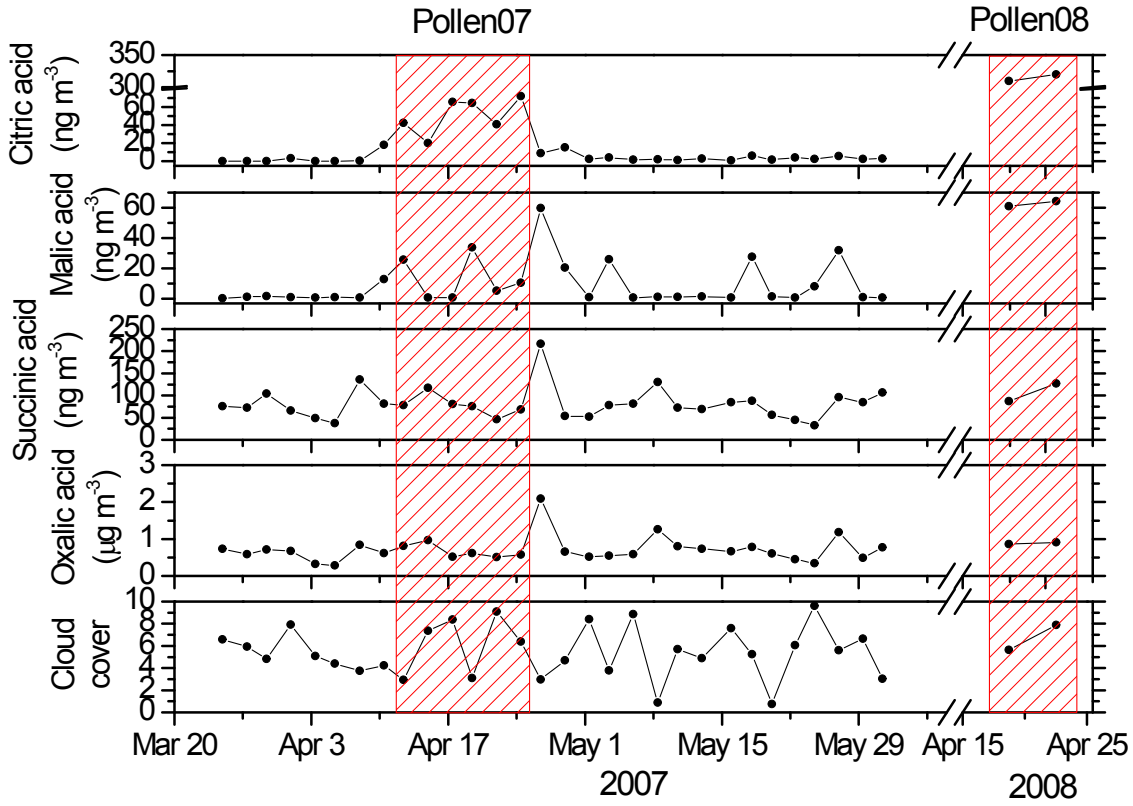

Pollen07
Pollen08
Citric acid (ng m-3)
Malic acid (ng m-3)
Succinic acid (ng m-3)
Oxalic acid (µg m-3)
Cloud cover
Mar 20
Apr 3
Apr 17
May 1
May 15
May 29
Apr 15
Apr 25
2007
2008

Figure 3

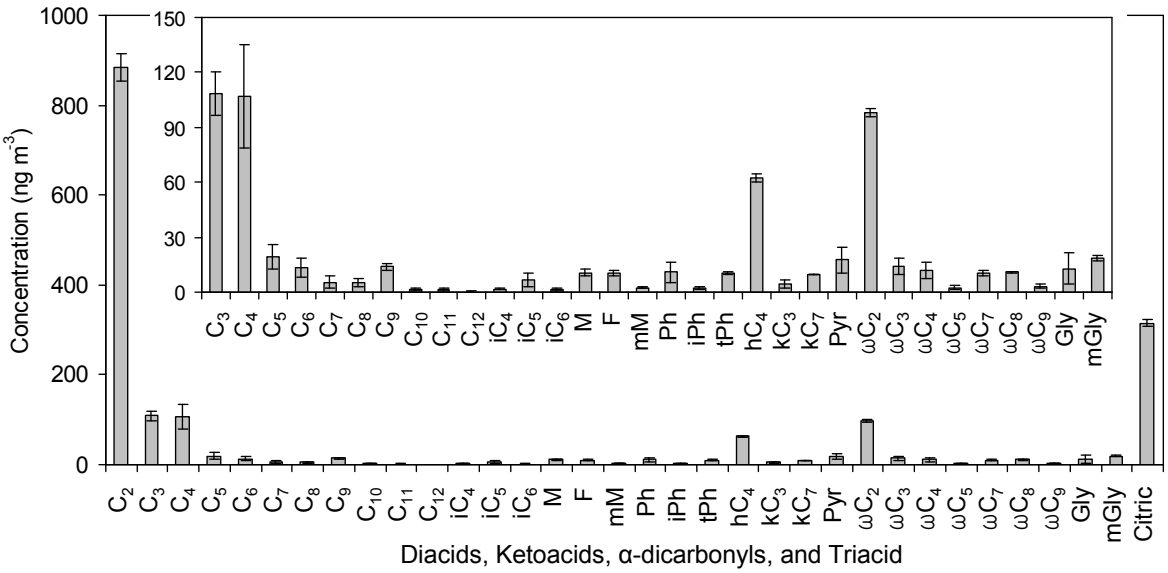

Concentration (ng m-3)
1000
800
600
400
200
0
150
120
90
60
30
0
C2 C3 C4 C5 C6 C7 C8 C9 C10 C11 C12 iC4 iC5 iC6 M F mM Ph iPh tPh hC4 kC3 kC7 Pyr ωC2 ωC3 ωC4 ωC5 ωC7 ωC8 ωC9 Gly mGly Citric
Diacids, Ketoacids, α-dicarbonyls, and Triacid

Figure 4

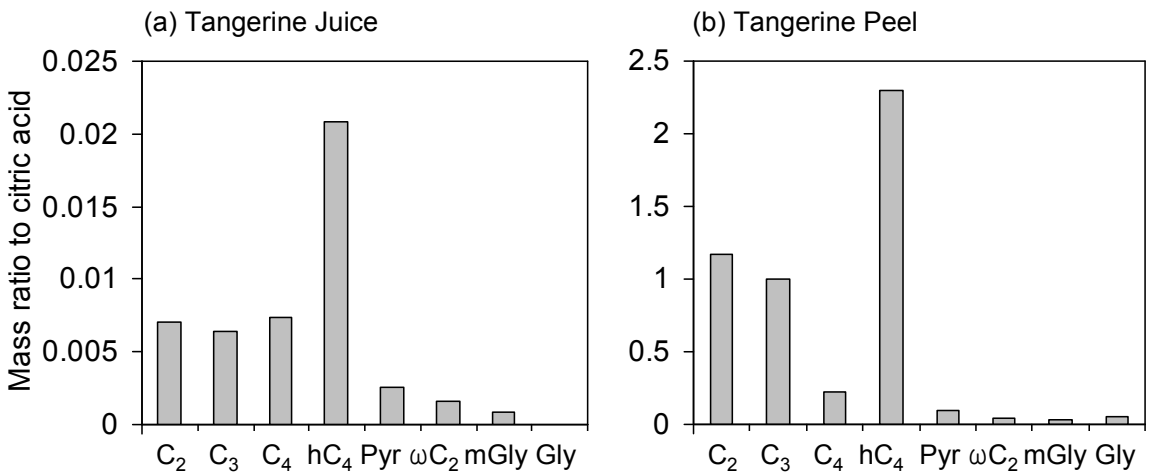

(a) Tangerine Juice
(b) Tangerine Peel
Mass ratio to citric acid
0.025
0.02
0.015
0.01
0.005
0
2.5
2
1.5
1
0.5
0
C2 C3 C4 hC4 Pyr ωC2 mGly Gly
C2 C3 C4 hC4 Pyr ωC2 mGly Gly

Figure 5

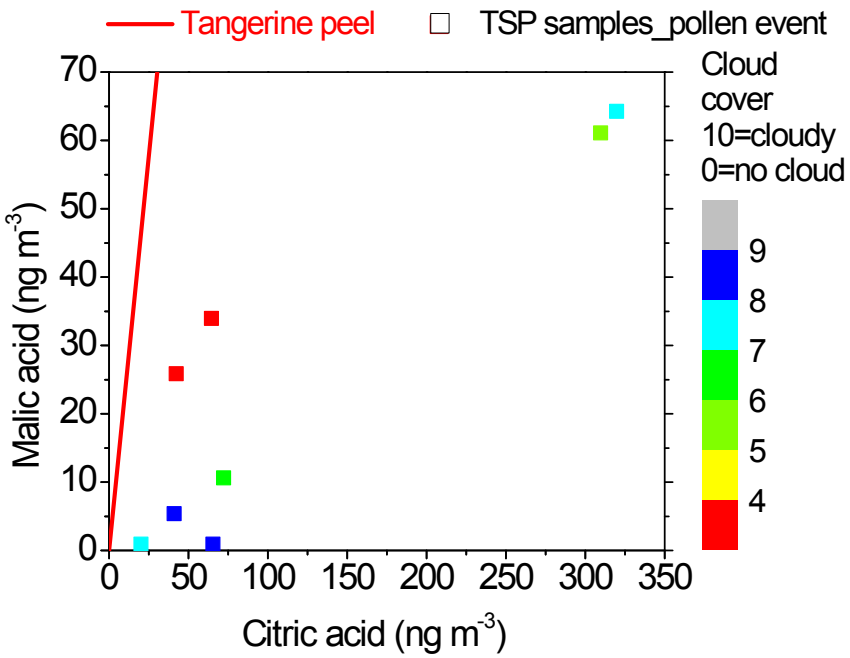

Tangerine peel
TSP samples_pollen event
Cloud cover
10=cloudy
0=no cloud
9
8
7
6
5
4
Malic acid (ng m-3)
Citric acid (ng m-3)
0
10
20
30
40
50
60
70
0
50
100
150
200
250
300
350

Figure 6

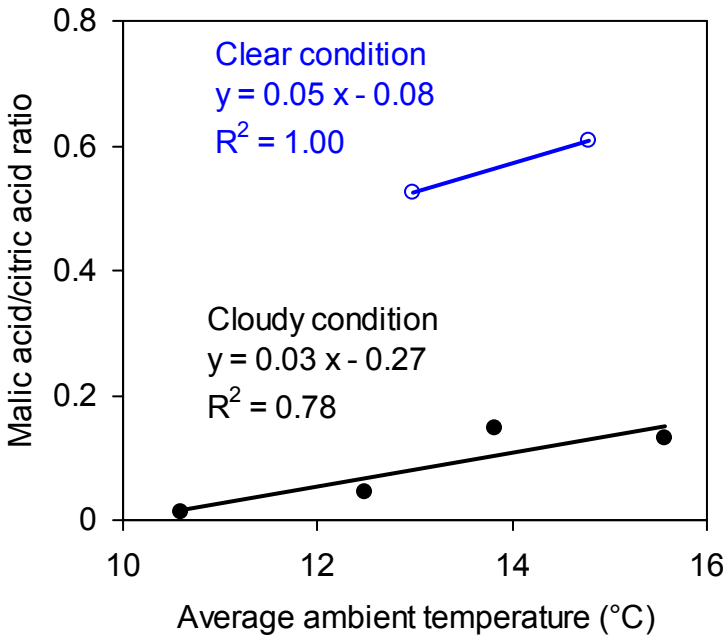
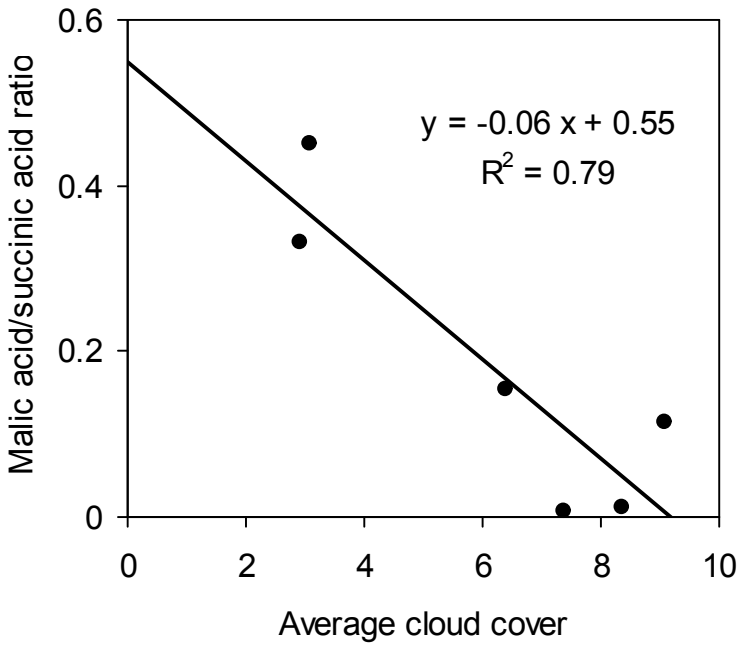

Clear condition
y = 0.05 x - 0.08
R2 = 1.00
Cloudy condition
y = 0.03 x - 0.27
R2 = 0.78
Malic acid/citric acid ratio
0.8
0.6
0.4
0.2
0
10
12
14
16
Average ambient temperature (°C)

Figure 7


0.6
0.4
0.2
0
Malic acid/succinic acid ratio
y = -0.06 x + 0.55
R2 = 0.79
0
2
4
6
8
10
Average cloud cover