

## Polar organic tracers in PM<sub>2.5</sub> aerosols from forests in eastern China

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**Abstract.** Photooxidation products of biogenic volatile organic compounds, mainly isoprene and monoterpenes, are significant sources of atmospheric particulate matter in forested regions. The objectives of this study were to examine time series and diel variations of polar organic tracers for the photooxidation of isoprene and  $\alpha$ -pinene to investigate whether they are linked with meteorological parameters or trace gases, and to determine their carbon contributions. In addition, the biogenic secondary organic carbon contributions from isoprene were estimated. PM<sub>2.5</sub> (particulate matter with an aerodynamic diameter  $<2.5 \mu\text{m}$ ) aerosol samples were collected from forests in eastern China and compared with data from forested sites in Europe and America. Aerosol sampling was conducted at four sites located along a gradient of ecological succession in four different regions, i.e. Changbai Mountain Nature Reserve (boreal-temperate), Chongming National Forest Park (temperate), Dinghu Mountain Nature Reserve (subtropical) and Jianfengling Nature Reserve in Hainan (tropical) during summer periods when the meteorological conditions are believed to be favorable for photochemical processes. Fifty PM<sub>2.5</sub> samples were collected; eighteen organic compounds, organic carbon (OC), elemental carbon and trace gases were measured. Results indicate that the concentration trends of the secondary organic compounds reflected those of the trace gases and meteorological parameters. Very good correlations between the sum concentrations of isoprene oxidation products and atmo-

spheric SO<sub>2</sub>, O<sub>3</sub>, NO<sub>2</sub>, NO<sub>x</sub>, as well as CO<sub>2</sub>, at the Changbai site were found. The secondary OC due to isoprene was relatively high in tropical Hainan ( $0.27 \mu\text{gC/m}^3$ ) where isoprene-emitting broadleaf species are dominant, but was comparable in boreal Changbai ( $0.32 \mu\text{gC/m}^3$ ) where coniferous species are prevalent. The contribution of malic acid, which may have both biogenic and anthropogenic sources, to the OC mass was comparable at the four sites.

### 1 Introduction

Vegetation releases numerous volatile organic compounds (VOCs) into the atmosphere, particularly isoprene, monoterpenes, and sesquiterpenes, as well as a series of oxygen-containing compounds (Fehsenfeld et al., 1992; Sharkey and Yeh, 2001). Knowledge of the atmospheric fate of these biogenic VOCs (BVOCs) is important because of the large quantities emitted globally compared with those of anthropogenic VOCs as well as their high reactivity (Hoffmann et al., 1997; Griffin et al., 1999). Secondary organic aerosol (SOA) is formed in the troposphere from the oxidation of BVOCs through reactions with ozone and OH or NO<sub>3</sub> radicals, where the resultant low-vapor-pressure oxidation products partition between the gas and aerosol phases or undergo further heterogeneous reactions in the aerosol phase (for a review, see Kanakidou et al., 2005). SOA produced over forests has received considerable attention for different reasons: it impairs visibility and may affect climate by scattering and absorbing solar radiation and by serving as cloud condensation nuclei.



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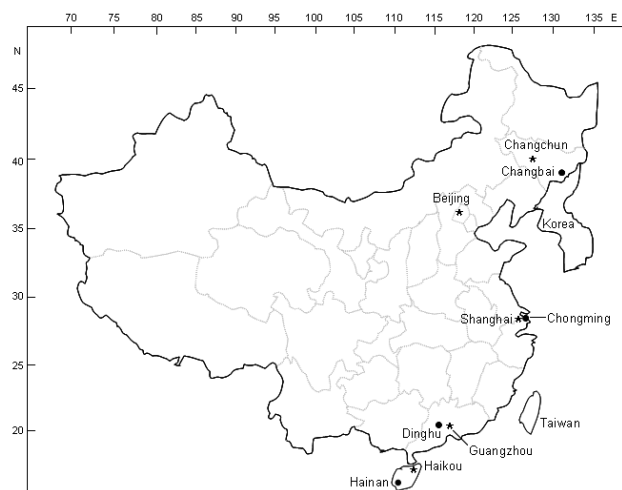


Fig. 1. Location of the sampling sites (denoted with filled circles).

China is comparable in size to Europe; hence, the isoprene and monoterpene emissions from China's ecosystems may be nearly the same as those for Europe (Klinger et al., 2002). So far, detailed organic speciation studies including oxidation products of isoprene and  $\alpha$ -pinene have mainly been conducted for forested sites in Europe and America, e.g. Hungary (Ion et al., 2005), Germany (Plewka et al., 2006; Böge et al., 2006; Kourtchev et al., 2008a), Finland (Kourtchev et al., 2005; Kourtchev et al., 2008b), the United States of America (USA) (Edney et al., 2005; Xia and Hopke, 2006; Cahill et al., 2006; Clements and Seinfeld, 2006; Lewandowski et al., 2007) and Brazil (Schkolnik et al., 2005). Information is available on the chemical composition of urban PM<sub>2.5</sub> organic aerosol from Beijing (He et al., 2006), Shanghai (Feng et al., 2006), Nanjing (Wang et al., 2005), inland and east coastal China (Wang et al., 2007), and 14 cities in China (Ho et al., 2007). However, detailed organic composition studies on fine aerosol from forested sites in China are lacking, except for a very recent study carried out in Hong Kong (Hu et al., 2008).

The objectives of the current study were to obtain insights into aerosol sources and source processes that lead to fine aerosol formation above Chinese forests, and to assess the biogenic secondary organic carbon (SOC) from isoprene. With regard to the latter contributions, estimates were made based on the measured SOA tracer concentrations and the laboratory-derived tracer mass fraction reported by Kleindienst et al. (2007). Day- and night-time and also 24-h PM<sub>2.5</sub> aerosol samples were collected along latitude in boreal, temperate, subtropical, tropical ecosystems, during summer periods when the meteorological conditions are favorable for photochemical reactions of BVOCs. The concentrations of oxidation products of isoprene and  $\alpha$ -pinene as well as of other marker compounds that provide information on aerosol sources, i.e. fungal spores (Lewis

and Smith, 1967; Bielecki, 1982) (arabitol, mannitol), plant pollen (Pacini, 2000) (glucose and fructose), wood combustion (Simoneit, 2002) (levoglucosan), and the oxidation of unsaturated fatty acids (Kawamura and Ikushima, 1993; Yu et al., 2005) (malic acid), were measured. As regards to oxidation products of isoprene, the following marker compounds were included: 2-methyltetrols (2-methylthreitol and 2-methylerythritol), C<sub>5</sub>-alkene triols [2-methyl-1,3,4-trihydroxy-1-butene (*cis* and *trans*) and 3-methyl-2,3,4-trihydroxy-1-butene] and 2-methylglyceric acid. Both the 2-methyltetrols (Claeys et al., 2004a) and the C<sub>5</sub>-alkene triols (Wang et al., 2005) were first characterized in fine tropical rainforest aerosol collected from the Amazon basin, Brazil, while 2-methylglyceric acid was first reported in rural fine aerosol collected from a deciduous/coniferous forest site in K-puszt, Hungary (Claeys et al., 2004b). In subsequent laboratory studies (Edney et al., 2005; Böge et al., 2006; Surratt et al., 2006), it was confirmed that these compounds are formed from the photooxidation of isoprene. As regards to marker compounds for the photooxidation of  $\alpha$ -pinene, pinic acid, norpinic acid, 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid were considered. These compounds have been reported in both field and smog chamber studies (Claeys et al., 2007); however, it is worth noting that the chemical structure of 3-methyl-1,2,3-butanetricarboxylic acid, which is believed to be a stable end-oxidation product formed through further oxidation of pinonic acid, was only recently elucidated (Szmigielski et al., 2007).

## 2 Experimental section

### 2.1 Site descriptions and sample collection

Study sites were located in four forests in eastern China along the north latitude from 42° to 18° (see Fig. 1). The boreal-temperate Changbai Mountain Forest Ecosystem Research Station (42°24'N, 128° 28'E, 763 m a.s.l., Jilin Province) is surrounded by 200 km<sup>2</sup> of condensed pine/hardwood forest (the region of Changbai Mountain Nature Reserve) with dominant species as pine (*Pinus koraiensis*), oak (*Quercus mongolica*), spruce (*Picea koreana*) and maple (*Acer mono*), etc. It is about 680 km to the west of Changchun (with a population of about 7 million), the capital city of Jilin province. This site is called Changbai, hereafter.

The temperate site was inside a water fir (*Metasequoia glyptostroboides* Hu and Cheng) plantation in the Dongping National Forest Park (30°50'N, 121°40'E, ~0 m a.s.l., Chongming island, Shanghai). It has an area of about 3 km<sup>2</sup> and is surrounded by orchard and grassland, and is 28 km away from Shanghai Municipal center (about 20 million inhabitants). This site is called Chongming, hereafter.

The subtropical Dinghu Mountain Forest Ecosystem Research Station (23°10'N, 112°32'E, 320 m a.s.l., Guangdong Province) is a monsoon evergreen broadleaf forest with some

needle tree species covering an area of about 11 km<sup>2</sup>. The vegetation mainly consists of hairy chestnut (*Castanopsis chinensis Hance*), Chinese cryptocarya (*Cryptocarya chinensis*), white gironniera (*Gironniera subaequalis Planch*) and schima (*Schima superba Gardn. Et Champ*). It is situated about 85 km to the west of Guangzhou (the capital city of Guangdong Province with a population of 7.5 million). This site is called Dinghu, hereafter.

The fourth site was in the Jianfengling Long-term Research Station of Tropical Forest Ecosystem (18°40'N, 108°49'E, 820 m a.s.l., Hainan Province). It is a tropical evergreen monsoon forest with an area of 475 km<sup>2</sup>, dominated by the species narig (*Vatica mangachapoi*), white olive (*Canarium album*) and white tea (*Coelodepas hainanensis*). It is about 315 km from Haikou, the capital city of Hainan Province. This site is called Hainan, hereafter. The central and western parts of Hainan island are mainly mountainous. The whole mountain area has an unsymmetrical circular distribution, which makes that the sampling site is situated in a rain forest basin. Therefore, the concentration of SOA from the photooxidation of isoprene is expected to be high at this site, unlike at coastal sites.

All sampling periods were selected taking into account the meteorological conditions and the maximum solar radiation, as well as high temperatures. The sampling periods were 23–29 July 2007 in Changbai, 12–19 June 2006 in Chongming, 2–14 August 2006 in Dinghu, and 20–27 November 2006 during the dry season in Hainan. In the case of Dinghu, the sampler was installed at the hilltop of the Dinghu Mountain Biosphere Reserve, which is a station supported by the Man and the Biosphere Program of the United Nations Educational, Scientific and Cultural Organization; only 24-h samples could be collected at this site for safety reasons.

For each site, two high-volume PM<sub>2.5</sub> air samplers (Graseby-Andersen) operated at a flow rate of 1.13 m<sup>3</sup> min<sup>-1</sup> were used, one collected day-/night-time samples (06:30 to 18:00 for day-time, 18:30 to 06:00 for night-time sampling), while the other collected 24-h samples, except at Dinghu where only 24-h samples were obtained. Whatman quartz fiber filters of 20.3 × 25.4 cm were used. Blank filters were obtained in the same way as the samples except that the collection time was only 15 s. No aerosol collection was performed on rainy days. In total, 50 field samples and 12 blanks were obtained.

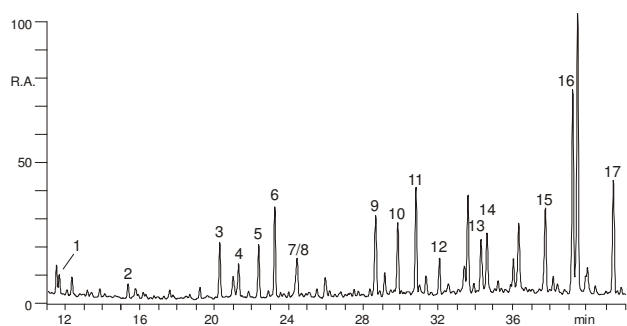
## 2.2 Meteorological parameters and trace gases

Meteorological parameters (i.e. temperature, wind speed, relative humidity, and altitude) were measured by a Kestrel 4000 Pocket Weather meter (Nielsen-Kelleman, USA). In the case of the Changbai site, measurements of O<sub>3</sub>, SO<sub>2</sub>, NO, NO<sub>2</sub>, NO<sub>x</sub> and CO<sub>2</sub> were performed simultaneously with Thermo Environmental Instruments: an ultraviolet light absorption O<sub>3</sub> analyzer (TEI 49C), a fluorescence SO<sub>2</sub> analyzer (TEI 43C), a chemiluminescence NO-NO<sub>2</sub>-NO<sub>x</sub> analyzer

(TEI 42C) and a gas filter correlation analyzer (TEI, model 41C), respectively. The Shanghai Environmental Monitoring Center supplied concentrations of SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub> for the Chongming site.

## 2.3 Aerosol analysis

Filter samples were analyzed for OC and elemental carbon (EC) by a thermo-optical transmission (TOT) technique (Birch and Cary, 1996). For analysis of polar organic compounds by gas chromatography/mass spectrometry (GC/MS), the samples were spiked with appropriate amounts of internal recovery standards (IS), i.e. 400 ng methyl-β-D-xylanopyranoside (MXP, Sigma) and 750 ng deuterated D<sub>3</sub>-malic acid (DMA, CDN isotopes, Canada), extracted with methanol, and derivatized with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA)+1% trimethylchlorosilane (TMCS) (Pierce) and anhydrous pyridine (2:1, v/v). Details about the sample workup procedure can be found in Kourtchev et al. (2008b). The GC/MS instrument consisted of a Hewlett-Packard model 6890 gas chromatograph equipped with a DP-5MS (30 m × 0.25 mm i.d., 0.25 μm film thickness), coupled to a Hewlett-Packard model 5975 MSD quadrupole analyzer. Data were acquired and processed with ChemStation software (Hewlett-Packard). The temperature program was as follows: initial temperature at 100°C held for 2 min, a gradient of 3°C min<sup>-1</sup> up to 200°C, held for 5 min, then 30°C min<sup>-1</sup> up to 310°C, held for 2 min. The mass spectrometer was operated in the electron ionization mode at 70 eV and an ion source temperature of 200°C. Full scan mode was used in the mass range *m/z* 50–650. Individual compounds were identified by comparison of mass spectra with those of authentic standards or literature data (Claeys et al., 2004a; Wang et al., 2004; Wang et al., 2005; Claeys et al., 2007). Selected ion monitoring mode was used for quantitative analysis and ion dwell time was 100 ms. Base ion fragments of *m/z* 204 and 217 for MXP, levoglucosan and sugars, *m/z* 219 and 277 for 2-methyltetrols, *m/z* 231 for C<sub>5</sub> alkene triols, *m/z* 233 and 307 for malic acid, *m/z* 236 and 310 for DMA, *m/z* 217 and 319 for arabitol and mannitol, *m/z* 349 for glutaric acid and *m/z* 405 for 3-methyl-1,2,3-butanetricarboxylic acid were monitored. For quantitative analysis, calibration curves were constructed by using authentic standards that were processed as described above. For the quantification of compounds that no standards were available the response factors of the following surrogate compounds were used: erythritol for 2-methyltetrols and C<sub>5</sub>-alkene triols, pinic acid for norpinic acid, 2-hydroxyglutaric acid for 3-hydroxyglutaric acid, and 1,4-cyclohexanedicarboxylic acid for 3-methyl-1,2,3-butanetricarboxylic acid.



**Fig. 2.** GC/MS total ion current chromatogram for the 24-h sample collected on 5 August 2007, in Dinghu: (1) 2-methylglyceric acid; (2) 3-methyl-2,3,4-trihydroxy-1-butene; (3) malic acid (+D<sub>3</sub>-malic acid (IS)); (4) erythritol; (5) 2-methylthreitol; (6) 2-methylerythritol; (7) 2-hydroxyglutaric acid; (8) 3-hydroxyglutaric acid; (9) methyl- $\beta$ -D-xylanopyranoside (IS); (10) levoglucosan; (11) arabitol; (12) 3-methyl-1,2,3-butanetricarboxylic acid; (13) fructose<sub>1</sub>; (14) fructose<sub>2</sub>; (15) glucose<sub>1</sub>; (16) mannitol; (17) glucose<sub>2</sub>. Other intense peaks are from column bleeding. The subscripts 1 and 2 after fructose and glucose denote different isomers.

### 3 Results and discussion

Figure 2 shows a typical total ion current GC/MS chromatogram for the 24-h sample collected on 5 August 2007 in Dinghu. It can be seen that intense peaks are detected for malic acid, 2-methylthreitol, 2-methylerythritol, 3-hydroxyglutaric acid, levoglucosan, arabitol, 3-methyl-1,2,3-butanetricarboxylic acid, fructose, mannitol and glucose. Small peaks corresponding to the other analytes could be visualized with extracted ion chromatography (not shown). A summary of the average concentrations and concentration ranges of OC, EC, organic compounds, and trace gases for 24-h, day-time and night-time PM<sub>2.5</sub> aerosol samples, and meteorological data for the four forest sites is listed in Table 1.

#### 3.1 Isoprene oxidation products

Significant amounts of the 2-methyltetrols, marker compounds for the photooxidation of isoprene, were observed in boreal-temperate Changbai, subtropical Dinghu and tropical Hainan with average concentrations of 49 ng/m<sup>3</sup>, 25 ng/m<sup>3</sup> and 41 ng/m<sup>3</sup>, and concentration ranges between 22–109 ng/m<sup>3</sup>, 3.5–84 ng/m<sup>3</sup>, 16–67 ng/m<sup>3</sup> for 24-h samples, respectively. These values are comparable to the average concentration of the 24-h Hi-Vol samples from Potsdam, NY, during June and August of 2005 (~50 ng/m<sup>3</sup>) (Xia and Hopke, 2006), and of the 48-h low-volume samples from Hyytiälä, Finland during a 2004 summer period (26 ng/m<sup>3</sup>) (Kourtchev et al., 2005).

For the Changbai and Hainan sites where 12-h samples were collected, the day-time average concentration of the 2-methyltetrols was 131 ng/m<sup>3</sup> and 60 ng/m<sup>3</sup>, while the corre-

sponding night-time average concentration was 113 ng/m<sup>3</sup> and 50 ng/m<sup>3</sup>, respectively. This phenomenon can be regarded as evidence for the fast photochemical formation of 2-methyltetrols from locally emitted isoprene. Interestingly, the contributions of the 2-methyltetrols to the OC mass were quite comparable for the two sites despite the differences in the vegetation (i.e. for Changbai: 2.3% during day-time, 1.9% at night; for Hainan: 2.2% during day-time, 1.6% at night). This indicates that at both sites the highest contribution of the 2-methyltetrols to the OC mass was found during day-time. It is also noted that the highest 24-h average concentrations were found for these sites (Table 1). The day-time maximum 2-methyltetrol concentration in Hainan was 86 ng/m<sup>3</sup>, while the night-time maximum was 92 ng/m<sup>3</sup>, corresponding to % contributions to the OC mass of 2.9% and 1.6%, respectively, which is in full agreement with the diel variation trend pointed out above. While the day-time average concentration of the 2-methyltetrols of 60 ng/m<sup>3</sup> for the tropical rain forest site Hainan is similar to the day-time concentration of 65 ng/m<sup>3</sup> in Balbina, Brazil (Claeys et al., 2004a), the day-time average 2-methyltetrol concentration of 131 ng/m<sup>3</sup> in boreal-temperate Changbai is much higher than that of 15.7 ng/m<sup>3</sup> in boreal forest at Hyytiälä, Finland, during a 2005 summer period (Kourtchev et al., 2008b). This also holds for the night-time 2-methyltetrol concentration, 113 ng/m<sup>3</sup>, which is much higher than the concentration of 10.3 ng/m<sup>3</sup> in Hyytiälä at night. This may be due to differences in latitude, vegetation types, leaf surface area and concentrations of trace gases in the atmosphere. The lower latitude of Changbai (42°24'N) compared to Hyytiälä (61°51'N) implies that there is more solar radiation and a higher temperature in Changbai (average 25.7°C in Changbai, 15.9°C in Hyytiälä, see Table 1). As to isoprene emissions from the vegetation, Yan et al. (2005) estimated that the annual biogenic isoprene emission is about 4.8 Tg C in whole China, and found that its spatial distribution corresponds with that of the vegetation. The highest annual emission flux exceeded 5000 kg C/km<sup>2</sup> in northeastern China, including Changbai Mountain, and in Hainan island (southeast). As to trace gases, the concentration of SO<sub>2</sub>, which is photooxidized to sulfuric acid and thought to be crucial in the formation of 2-methyltetrols, was 2.29 ppbv in Changbai compared to 0.04 ppbv in Hyytiälä. Therefore, the combined effects of higher isoprene emissions, higher photo-activity and higher concentrations of SO<sub>2</sub> may explain the fairly high maximum 2-methyltetrol concentration (282 ng/m<sup>3</sup>) in Changbai during day-time.

Furthermore, the C<sub>5</sub>-alkene triols, compounds related to the 2-methyltetrols, were also detected at the four study sites. Their diel variations roughly follow those of the 2-methyltetrols. Recently, C<sub>5</sub>-alkene triols and 2-methyltetrols were both reported to be generated from isoprene under low-NO<sub>x</sub> conditions and are believed to be formed through reaction of isoprene with the OH radical. In addition, the formation of C<sub>5</sub>-alkene triols was explained through rearrangement

**Table 1.** Average concentrations and concentration ranges of OC, EC, organic compounds, trace gases for day-time, night-time and 24-h PM<sub>2.5</sub> samples collected in Changbai, Chongming, Dingdu and Hainan, and meteorological data.

Species	24-h		Day-time		Night-time	
	Average	Conc. Range	Average	Conc. Range	Average	Conc. Range
Boreal-temperate, Changbai (23–29 July 2007)						
	<i>n</i> =5		<i>n</i> =5		<i>n</i> =4	
OC (μg/m <sup>3</sup> )	4.8	3.6~5.7	5.6	3.3~6.7	6.1	5.1~6.9
EC	0.41	0.32~0.52	0.48	0.28~0.58	0.52	0.44~0.59
Organic compounds (ng/m <sup>3</sup> )						
2-methylthreitol	16.7	4.7~37	35	14.2~80	26	6.9~45
2-methylerythritol	32	17.6~72	96	55~202	86	24~118
∑ 2-methyltetrols	49	22~109	130	69~282	113	31~144
C <sub>5</sub> -alkene triols	4.4	0.19~11	10	0.23~28	1.2	n.d~3.3
2-methylglyceric acid	0.50	n.d~2.5	3.0	n.d~12	–	–
∑ isoprene oxidation products	53	23~120	140	69~290	114	31~166
3-hydroxyglutaric acid	17	7.7~27	16	*	25	*
3-methyl-1,2,3-butanetricarboxylic acid	14	8.5~18	22	*	16	*
∑ α-pinene oxidation products	31	16~46	38	*	41	*
malic acid	44	31~63	77	65~88	109	*
levoglucosan	42	32~67	38	27~66	68	23~103
arabitol	6.9	0.99~11	11	n.d~35	5.3	n.d~16
mannitol	30	12~66	32	24~46	49	21~87
fructose	5.2	3.9~7.2	15	6.5~25	96	4.6~278
glucose	51	16~149	77	21~111	323	25~672
threitol	1.3	n.d~4.1	0.57	n.d~1.5	2.9	n.d~8.8
erythritol	1.9	0.054~4.4	1.2	0.71~2.01	4.9	n.d~14
2-hydroxyglutaric acid	15	13~18	48	*	18	*
SUM	239	99~343	384	252~532	730	108~1479
Trace gases (ppbv)						
SO <sub>2</sub>	2.04	1.7~7.1	2.3	1.7~4.1	1.8	1.7~2.6
NO	0.35	0.15~1.8	0.28	0.15~2.8	0.4	0.15~2.8
NO <sub>2</sub>	0.47	n.d~6.4	0.66	n.d~4.2	0.60	0.01~4.2
NO <sub>x</sub>	0.67	0.05~6.4	0.92	0.05~7.0	0.93	0.24~7.0
O <sub>3</sub>	31	0.25~60	43	12~75	25	0.25~53
CO <sub>2</sub> (ppmv)	456	447~473	436	421~448	485	476~501
Meteorological parameters						
Temperature (°C)	25	22~27	26	24~27	23	21~24
Wind speed (m/s)	0.27	0.12~0.48	0.57	0.09~1.2	0.17	0.10~0.25
Relative humidity (%)	59	44~74	64	56~76	72	63~77

reactions of hydroxyhydroperoxy radicals that are formed in the initial photooxidation reaction of isoprene (Surratt et al., 2006). The maximum sum concentration of the three C<sub>5</sub>-alkene triol isomers was 10 ng/m<sup>3</sup> and 19.3 ng/m<sup>3</sup> in Changbai and Hainan, respectively. The ratio of the concentrations of C<sub>5</sub>-alkene triols and 2-methyltetrols was 1:13 in Changbai versus 1:3 in Hainan. The highest ratio and highest concentrations of 2-methyltetrols were thus found for Changbai. A possible explanation for this observation is that different mechanisms may result in the formation of 2-methyltetrols;

while the formation of 2-methyltetrols likely mainly involves low-NO<sub>x</sub> conditions (Surratt et al., 2006) at the tropical Hainan site, that at the more polluted Changbai site may also involve additional pathways such as sulfuric acid-catalyzed formation (Edney et al., 2005; Surratt et al., 2007b) (see further discussion). 2-methylglyceric acid, another marker compound for the photooxidation of isoprene, was only found at very low concentrations in this study (Table 1).

Table 1. Continued.

Species	24-h		Day-time		Night-time	
	Average	Conc. Range	Average	Conc. Range	Average	Conc. Range
Temperate, Chongming (12–19 June 2006)						
	<i>n</i> =4		<i>n</i> =4		<i>n</i> =1 <sup>#</sup>	
OC (μg/m <sup>3</sup> )	9.9	5.8~15	10.5	6.4~17	5.0	*
EC	1.7	0.98~2.6	1.8	1.1~2.8	0.84	*
Organic compounds(ng/m <sup>3</sup> )						
2-methylthreitol	1.4	0.87~2.3	1.7	0.4~3.4	1.6	*
2-methylerythritol	3.0	2.2~4.3	4.3	1.4~8.1	4.2	*
∑ 2-methyltetrols	4.4	3.1~6.6	6.0	1.8~12	5.8	*
C <sub>5</sub> -alkene triols	0.09	n.d~0.23	0.10	n.d~0.22	0.7	*
2-methylglyceric acid	0.33	n.d~0.95	–	–	–	–
∑ isoprene oxidation products	4.8	3.1~7.8	6.1	1.8~12	6.6	*
3-hydroxyglutaric acid	–	–	–	–	–	–
norpinic acid	1.8	n.d~3.6	–	–	–	–
3-methyl-1,2,3-butanetricarboxylic acid	–	–	–	–	–	–
∑ α-pinene oxidated products	1.8	n.d~3.6	–	–	–	–
malic acid	58	37~88	79	16~173	32	*
levoglucosan	143	20~212	40	2.5~112	17	*
arabitol	0.72	0.28~1.4	2.9	0.18~8.4	0.69	*
mannitol	1.9	0.43~4.6	5.8	1.5~12	1.3	*
fructose	1.3	0.78~2.1	4.3	2.1~8.3	1.9	*
glucose	2.4	0.73~4.2	10.3	2.0~25	2.1	*
threitol	0.95	0.073~1.7	0.39	n.d~1.0	0.042	*
erythritol	0.61	0.40~0.90	0.80	0.05~2.2	3.3	*
SUM	74	82~111	109	25~242	48	*
Trace gases (ppbv)						
SO <sub>2</sub>	10	7.0~17	16	8.0~27	23	*
NO <sub>2</sub>	22	13~22	25	18~34	36	*
O <sub>3</sub>	43	33~57	34	15~54	21	*
Meteorological parameters						
Temperature (°C)	29	29~30	27	26~28	27	*
Wind speed (m/s)	0.7	0.4~1.2	0.5	0.32~0.78	0.25	*
Relative humidity (%)	68	60~75	73	64~80	82	*

The sum concentration of the 2-methyltetrols in 24-h samples from Changbai shows a good correlation with SO<sub>2</sub> ( $r^2=0.9455$ ) (Fig. 2). In addition, 2-methyltetrols are well correlated with ozone ( $r^2=0.982$ ) during day-time, and with NO<sub>2</sub> ( $r^2=0.9618$ ) and NO<sub>x</sub> ( $r^2=0.8805$ ) at night. Similar results were obtained for the Chongming site (not shown, insufficient data points). The good correlation between the concentrations of the 2-methyltetrols and SO<sub>2</sub> (which is oxidized to sulfuric acid) is consistent with sulfuric acid playing a crucial role in the formation of the 2-methyltetrols (Edney et al., 2005; Surratt et al., 2007b). It cannot be ruled out that part of the 2-methyltetrols were originally present in the samples as sulfate esters which are also known to occur in ambient aerosol; these sulfate ester derivatives will be

measured as 2-methyltetrols with the derivatization GC/MS method employed in the present study (Surratt et al., 2007a, 2007b, 2008; Gómez-González et al., 2008).

As regards to the good correlation found for the concentrations of the 2-methyltetrols and NO<sub>2</sub> at night, a recent smog chamber study by Ng et al. (2008) demonstrated that nitrate derivatives of the 2-methyltetrols can be formed through night-time NO<sub>3</sub> radical chemistry; these nitrate derivatives will not be stable upon derivatization GC/MS and will also be measured as 2-methyltetrols. Interestingly, the day-time 2-methyltetrol concentrations show a reverse correlation with CO<sub>2</sub> (Fig. 3;  $r^2=0.9467$ ). A good correlation was found between the 2-methylthreitol and 2-methylerythritol concentrations for the four sites (the  $r^2$  value for Changbai,

Table 1. Continued.

Species	24-h		Day-time		Night-time	
	Average	Conc. Range	Average	Conc. Range	Average	Conc. Range
Subtropical, Dinghu (2–14 August 2006)						
<i>n</i> =7						
OC ( $\mu\text{g}/\text{m}^3$ )	5.1	1.8~8.0				
EC	0.69	0.25~1.1				
Organic compounds ( $\text{ng}/\text{m}^3$ )						
2-methylthreitol	5.7	1.3~13				
2-methylerythritol	20	2.2~70				
$\sum$ 2-methyltetrols	25	3.5~83				
C <sub>5</sub> alkene triols	0.62	0.14~1.51				
2-methylglyceric acid	0.09	n.d~0.18				
$\sum$ isoprene oxidation products	26	4.3~84				
3-hydroxyglutaric acid	–	–				
norpinic acid	–	–				
3-methyl-1,2,3-butanetricarboxylic acid	–	–				
$\sum$ $\alpha$ -pinene oxidation products	–	–				
malic acid	29	4.1~62				
levoglucosan	25	0.3~61				
arabitol	2.8	0.92~7.7				
mannitol	5.0	2.0~12				
fructose	8.8	1.3~37				
glucose	6.2	2.0~19				
threitol	0.21	n.d~0.51				
erythritol	3.1	0.22~18				
SUM	81	15~178				
Meteorological parameters						
Temperature ( $^{\circ}\text{C}$ )	24.2	24~28				
Wind speed (m/s)	0.57	0.26~0.90				
Relative humidity (%)	73.5	60~82				

Chongming, Dinghu and Hainan was 0.87, 0.94, 0.85 and 0.81, respectively) is consistent with their formation through the same aerosol source process, i.e. photooxidation of isoprene.

### 3.2 $\alpha$ -pinene oxidation products

The recently identified markers for SOA from the photooxidation of  $\alpha$ -pinene, i.e. 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid, were detected in samples from the boreal-temperate Changbai site. It is noted that at this site the concentration of the  $\alpha$ -pinene oxidation products is much lower than that of the isoprene oxidation products. The average 24-h concentrations of 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid were 17.2  $\text{ng}/\text{m}^3$  and 13.5  $\text{ng}/\text{m}^3$ , respectively, close to the values of 16.1  $\text{ng}/\text{m}^3$  and 13.5  $\text{ng}/\text{m}^3$  during July and August 2005 in Hyytiälä, Finland. In tropical Hainan, 3-methyl-

1,2,3-butanetricarboxylic acid could only be detected in 24-h samples, while norpinic acid was found at a concentration of 5  $\text{ng}/\text{m}^3$ , lower than 22.2  $\text{ng}/\text{m}^3$  reported for the Finnish samples. The concentration of 3-hydroxyglutaric acid in Hainan was 2.4  $\text{ng}/\text{m}^3$ , again lower than Changbai (17.2  $\text{ng}/\text{m}^3$ ) and Finland (16.1  $\text{ng}/\text{m}^3$ ). These differences can for a part be explained by differences in the vegetation along latitude with isoprene-emitting species dominating in tropical regions and  $\alpha$ -pinene-emitting species being prevalent in boreal regions. Pinic acid, a major photooxidation product of  $\alpha$ -pinene in laboratory experiments, could only be detected at trace levels in all samples. In this respect, it is noted that low to rather high concentrations of pinic acid (range: 0.4–135  $\text{ng}/\text{m}^3$ ) have been reported in field studies conducted at European and USA sites, including Pertouli in Greece (Kavouras et al., 1999a), Tábua in Portugal (Kavouras et al., 1999b), Hyytiälä in Finland (Kourtchev et al., 2005; Kourtchev et al., 2008b), the Blodgett forest in California, USA (Cahill et al., 2006),

Table 1. Continued.

Species	24-h		Day-time		Night-time	
	Average	Conc. Range	Average	Conc. Range	Average	Conc. Range
Tropical, Hainan (20–27 November 2006)						
	<i>n</i> =5		<i>n</i> =8		<i>n</i> =7	
OC ( $\mu\text{g}/\text{m}^3$ )	2.4	1.4~4.5	2.7	1.9~3.7	3.1	1.5~5.8
EC	0.20	0.12~0.38	0.23	0.17~0.32	0.20	0.12~0.38
Organics compounds ( $\text{ng}/\text{m}^3$ )						
2-methylthreitol	12	4.7~20	17	8.7~28	12	2.8~20
2-methylerythritol	29	11~48	43	27~65	38	8.2~71
$\Sigma$ 2-methyltetrols	41	15~67	60	36~86	50	11~92
C <sub>5</sub> -alkene triols	9.3	2.3~19	19	8.1~32	17	0.33~42
2-methylglyceric acid	0.74	0.21~1.2	0.66	0.11~1.2	0.74	0.26~2.4
$\Sigma$ isoprene oxidation products	51	19~87	80	49~119	68	12~123
3-hydroxyglutaric acid	2.4	1.1~4.4	3.1	3.0~3.2	2.8	2.2~3.4
norpinic acid	5.0	0.38~8.7	17	16~17	0.29	*
3-methyl-1,2,3-butanetricarboxylic acid	2.1	0.43~4.7	–	–	–	–
$\Sigma$ $\alpha$ -pinene oxidation products	9.4	6.5~15	20	19~20	2.9	2.2~3.4
malic acid	24	15~34	33	18~456	46	15~122
levoglucosan	107	19~398	29	14~41	153	4.4~437
arabitol	15	7.0~42	10	8.5~11	8.7	5.6~15
mannitol	16	7.9~47	15	11~23	8.6	3.8~18
fructose	12	4.6~43	10	6.9~12	4.7	1.4~14
glucose	22	9.5~61	20	9.9~33	7.1	4.3~13
threitol	0.89	0.30~2.9	0.55	0.39~0.80	1.0	0.11~2.3
erythritol	3.6	2.0~5.7	9.9	5.8~18	2.4	0.62~4.0
2-hydroxyglutaric acid	4.6	2.0~9.6	6.8	5.8~7.8	3.1	1.2~6.3
SUM	154	94~132	189	160~219	149	57~120.
Meteorological parameters						
Temperature ( $^{\circ}\text{C}$ )	22	20~25	24	21~27	23	20~26
Wind speed (m/s)	0.48	0.15~0.85	0.90	0.2~2.3	0.45	n.d~0.85
Relative humidity (%)	80	69~88	72	47~87	82	69~91

\* the compound was detectable in one sample, no concentration range was available.

– not detected, the detection limit was  $\sim 50 \text{ pg}/\text{m}^3$  for pinic acid,  $\sim 20 \text{ pg}/\text{m}^3$  for norpinic acid.

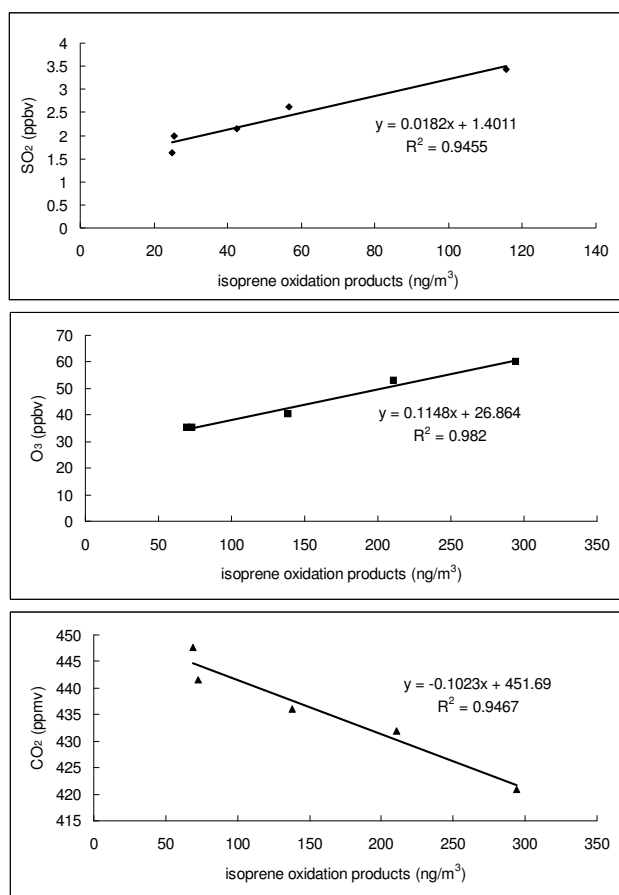
# one night sample was collected due to rain at Chongming.

the Fichtel mountains in Germany (Plewka et al., 2006), K-puszta in Hungary (Claeys et al., 2007), and Jülich in Germany (Kourchev et al., 2008a). At the Chongming site, only norpinic acid could be detected at low concentration ( $1.8 \text{ ng}/\text{m}^3$ ), while the relatively low sum concentration of isoprene oxidation products ( $4.7 \text{ ng}/\text{m}^3$ ) is probably due to isoprene emissions from surrounding orchards and less from coniferous water fir. No  $\alpha$ -pinene oxidation products could be detected in subtropical Dinghu, which is not surprising since the vegetation mainly consists of isoprene-emitting broadleaf tree species.

### 3.3 Other identified compounds

In contrast to isoprene and  $\alpha$ -pinene oxidation products, the concentrations of malic acid for Changbai, Chongming, Dinghu and Hainan were comparable, i.e.  $43.5 \text{ ng}/\text{m}^3$ ,  $58.3 \text{ ng}/\text{m}^3$ ,  $24.9 \text{ ng}/\text{m}^3$  and  $24.1 \text{ ng}/\text{m}^3$ , respectively, similar to  $46 \text{ ng}/\text{m}^3$  in Hyytiälä, Finland (Kourchev et al., 2005),  $39 \text{ ng}/\text{m}^3$  in K-puszta, Hungary (Ion et al., 2005),  $22 \text{ ng}/\text{m}^3$  in Balbina, Brazil (Claeys et al., 2004a), and  $39.1 \text{ ng}/\text{m}^3$  in Jülich, Germany (Kourchev et al., 2008a). The sugar alcohols, arabitol and mannitol, showed sum concentrations of  $36.9 \text{ ng}/\text{m}^3$ ,  $2.8 \text{ ng}/\text{m}^3$ ,  $7.8 \text{ ng}/\text{m}^3$  and  $30.8 \text{ ng}/\text{m}^3$  for Changbai, Chongming, Dinghu and Hainan, respectively. The sum concentrations of fructose and glucose were  $55.8 \text{ ng}/\text{m}^3$ ,  $3.6 \text{ ng}/\text{m}^3$ ,  $15.9 \text{ ng}/\text{m}^3$  and  $33.7 \text{ ng}/\text{m}^3$ , respectively. Both the



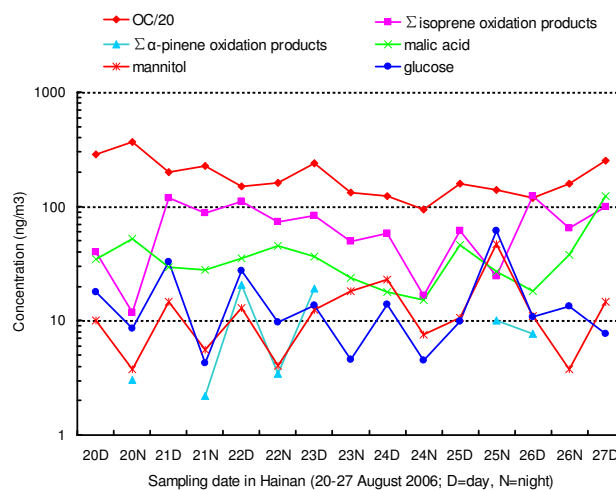


**Fig. 3.** Scatter plots of atmospheric concentration of SO<sub>2</sub> for 24-h (top), concentrations of O<sub>3</sub> (middle) and CO<sub>2</sub> (bottom) for the day-time versus the respective mass concentration of isoprene oxidation products (25–57 ng/m<sup>3</sup> for 24-h, 69–294 ng/m<sup>3</sup> for day-time sample) in Changbai.

latter sugar alcohols and sugars thus revealed substantial concentrations, as could be expected for ecosystems that are active during the considered periods.

### 3.4 Time series, OC/EC ratios, species attribution to OC, and secondary organic carbon contributions from isoprene

Figure 4 shows time series for OC and the measured species, isoprene and  $\alpha$ -pinene oxidation products, malic acid, mannitol and glucose, in Hainan. Isoprene oxidation products, mannitol (similar to arabitol) and glucose (similar to fructose) gave the same diel pattern with the highest concentration during day-time. Enhanced day-time isoprene oxidation products are consistent with the light- and temperature-dependent isoprene emission. Malic acid did not show day/night variations and followed closely the OC, indicating that its formation involves a longer time scale than that of isoprene oxidation products. Similar time series for the



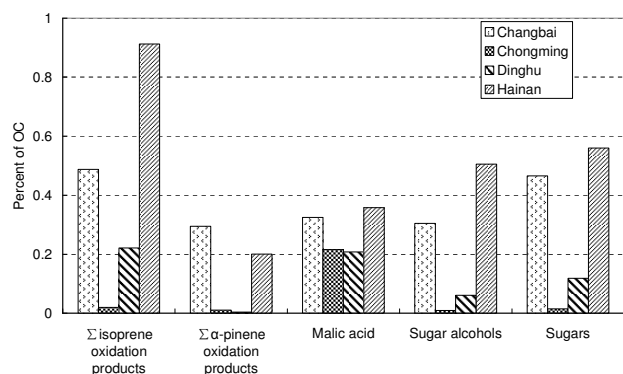
**Fig. 4.** Time trends for the concentrations of OC and selected compounds, i.e., isoprene oxidation products,  $\alpha$ -pinene oxidation products, malic acid, mannitol and glucose for day/night samples collected from Hainan.

2-methyltetrols, malic acid and mannitol have been reported for K-puszt, Hungary, during a 2003 summer period (Ion et al., 2005).

The higher OC/EC ratios ( $\sim 12$ ) for Changbai and Hainan indicate pristine forest regions that are mainly influenced by biogenic emissions, while the lower OC/EC ratios (5–6) for Chongming and Dinghu can be explained by EC contributions from traffic exhaust or biomass combustion. It is noted that both Chongming and Dinghu are in densely populated regions that are heavily impacted by traffic. With regard to the Chongming site, we could also conclude that the site was affected by biomass combustion during the sampling period, since high concentrations of levoglucosan, a wood combustion tracer (Simoneit, 2002), were measured (Table 1; average concentration 24-h samples, 143 ng/m<sup>3</sup>, range: 20–212 ng/m<sup>3</sup>). In addition, the high OC concentrations (on average 9.9  $\mu\text{g}/\text{m}^3$ ) found for Chongming can also be attributed to biomass burning.

Figure 5 shows the percentages of the OC attributable to the carbon in the organic compounds or groups of compounds for 24-h samples in Changbai, Chongming, Dinghu and Hainan. It can be seen that the OC attributable to isoprene SOA tracers is the highest in Changbai and Hainan (i.e. 0.49% and 0.91%), while that due to  $\alpha$ -pinene tracers is the highest in Changbai (0.30%), as could be expected for a boreal forest site. The contributions of malic acid to the OC for the four sites were comparable, while those of the sugars and the sugar alcohols were also the highest for Changbai and Hainan, consistent with active forest ecosystems.

The secondary organic carbon (SOC) contributions from isoprene were estimated using measured tracer concentrations and the laboratory-derived tracer mass fraction ( $f_{\text{SOC}}$ ) of  $0.155 \pm 0.039$  reported by Kleindienst et al. (2007). The



**Fig. 5.** Percentage of the OC attributable to the carbon in the organic compounds or groups of compounds for 24-h samples in Changbai, Chongming, Dinghu and Hainan.

same set of tracers for isoprene SOA (i.e. 2-methyltetrols and 2-methylglyceric acid) was used as those in the latter study. Using the tracer concentrations of the 24-h samples and the laboratory-derived  $f_{\text{SOC}}$  value, the SOC contributions from isoprene were estimated at  $0.32 \mu\text{gC}/\text{m}^3$  for Changbai,  $0.03 \mu\text{gC}/\text{m}^3$  for Chongming,  $0.16 \mu\text{gC}/\text{m}^3$  for Dinghu and  $0.27 \mu\text{gC}/\text{m}^3$  for Hainan. The highest SOC contributions from isoprene were thus found in tropical Hainan and boreal Changbai. With respect to the high value obtained for the boreal site, it is worth mentioning some coniferous species (e.g. *Picea abies*) are known to emit isoprene (Hakola et al., 2003). These values are about a factor of 4 lower than those reported for Research Triangle Park, southern USA, during the summer of 2003 (Kleindienst et al., 2007), but compare quite well with data that were recently reported for Hong Kong during a 2006 summer period (i.e.  $0.20 \mu\text{gC}/\text{m}^3$  on clean days and  $0.46 \mu\text{gC}/\text{m}^3$  on polluted days) (Hu et al., 2008). It was not possible in the present work to determine the SOC contributions from  $\alpha$ -pinene because not all tracers required to estimate this contribution were measured.

#### 4 Conclusions

It can be concluded that all measured biogenic tracer compounds show significant concentrations in both Hainan and Changbai. Isoprene photooxidation is an important process for SOA formation with the average 24-h oxidation products of isoprene in Hainan and Changbai contributing 0.91% and 0.49% to the OC, and the SOC from isoprene estimated at  $0.27 \mu\text{gC}/\text{m}^3$  and  $0.32 \mu\text{gC}/\text{m}^3$ , respectively. The maximum carbon contribution of isoprene and  $\alpha$ -pinene oxidation products to the OC was 2.4% ( $293 \text{ ng}/\text{m}^3$ , Changbai day-time) and 0.3% ( $41.3 \text{ ng}/\text{m}^3$ , Changbai night-time), respectively. For the boreal Changbai site,  $\alpha$ -pinene oxidation products contribute 0.30% to the OC, which is the highest for the four sites. The large part of the organic compounds that were not

extractable in methanol or not detectable by GC/MS such as oligomeric humic-like substances and biopolymeric material likely constitute a major fraction of the unidentified organic matter. More research is warranted to better characterize the latter large missing portion of the organic matter using analytical methodology that is complementary to GC/MS such as, for example, liquid chromatography/mass spectrometry with electrospray ionization detection. Considering that  $\text{SO}_2$  emissions are quite high in China, it would be very worthwhile to measure organosulfates of isoprene and  $\alpha$ -/ $\beta$ -pinene oxidation products that have only recently been reported (Surratt et al., 2007a, 2008; Iinuma et al., 2007; Gómez-González et al., 2008). In general, the chemical constituents of SOA and their concentrations depend on the vegetation area, plant species, meteorological conditions or trace gases. The correlation between  $\text{SO}_2$  and isoprene oxidation products supports that sulfuric acid plays an important role in the formation of isoprene-related SOA.

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#### References

- Bielecki, R. L.: Sugar alcohols, in: Encyclopedia of plant physiology, volume 13A, Plant Carbohydrates, volume I, Intracellular Carbohydrates, edited by Loewus, A., and Tanner, W., Springer-Verlag, Berlin, 158–170, 1982.
- Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, *Aerosol Sci. Technol.*, 25, 221–241, 1996.
- Böge, O., Miao, Y. K., Plewka, A., and Herrmann, H.: Formation of secondary organic particle phase compounds from isoprene gas-phase oxidation products: An aerosol chamber and field study, *Atmos. Environ.*, 40, 2501–2509, 2006.
- Cahill, T. M., Seaman, V. Y., Holzinger, R., and Goldstein, A. H.: Secondary organic aerosols formed from oxidation of biogenic volatile compounds in the Sierra Nevada mountains of California, *J. Geophys. Res.*, 111, D16312, doi:10.1029/2006JD007178, 2006.
- Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P., and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, 303, 1173–1176, 2004a.

- Claeys, M., Wang, W., Ion, A. C., Kourtchev, I., Gelencsér, A., and Maenhaut, W.: Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, *Atmos. Environ.*, 38, 4093–4098, 2004b.
- Claeys, M., Szmigielski, R., Kourtchev, I., Van der Veken, P., Vermeylen, R., Maenhaut, W., Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., and Edney, E. O.: Hydroxydicarboxylic acids: markers for secondary organic aerosols from the photooxidation of  $\alpha$ -pinene, *Environ. Sci. Technol.*, 41, 823–829, 2007.
- Clements, A. L. and Seinfeld, J. H.: Detection and quantification of 2-methyltetrols in ambient aerosol in the southeastern United States, *Atmos. Environ.*, 41, 1825–1830, 2006.
- Edney, E., Kleindienst, T., Jaoui, M., Lewandowski, M., Offenberg, J., Wang, W., and Claeys, M.: Formation of 2-methyltetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO/SO<sub>2</sub>/air mixtures and their detection in ambient PM<sub>2.5</sub> samples collected in the eastern United States, *Atmos. Environ.*, 39, 5281–5289, 2005.
- Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A. B., Hewitt, C. N., Lamb, B., Liu, S., Trainer, M., Westberg, H., and Zimmerman, P.: Emission of volatile organic compounds from vegetation and the implications for atmospheric chemistry, *Glob. Biogeochem. Cy.*, 6, 389–396, 1992.
- Feng, J., Chan, C., Fang, M., Hu, M., He, L., and Tang, X.: Characteristics of organic matter in PM<sub>2.5</sub> in Shanghai, *Chemosphere*, 64, 1393–1400, 2006.
- Gómez-González, Y., Surratt, J. D., Cuyckens, F., Szmigielski, R., Vermeylen, R., Jaoui, M., Lewandowski, M., Offenberg, J. H., Kleindienst, T. E., Edney, E. O., Blockhuys, F., Van Alsenoy, C., Maenhaut, W., and Claeys, M.: Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(–)electrospray ionization mass spectrometry, *J. Mass Spectrom.*, 43, 371–382, 2008.
- Griffin, R. J., Cocker III, D. R., Flagan, R. C., and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, *J. Geophys. Res.*, 104, 3555–3567, 1999.
- Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellen, H., and Keronen, P.: Seasonal variation of VOC concentrations above a boreal coniferous forest, *Atmos. Environ.*, 37, 1623–1634, 2003.
- He, L., Hu, M., Huang, X., Zhang, Y., and Tang, X.: Seasonal pollution characteristics of organic compounds in atmospheric fine particles in Beijing, *Sci. Total Environ.*, 359, 167–176, 2006.
- Ho, K., Cao, J., Lee, S., Kawamura, K., Zhang, R., Chow, J., and Watson, J.: Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China, *J. Geophys. Res.*, 112, D22S27, doi:10.1029/2006JD008011, 2007.
- Hoffmann, T., Odum, J. R., Bowman, F., Collins, D., Klockow, D., Flagan, R. C., and Seinfeld, J. H.: Formation of organic aerosols from the oxidation of biogenic hydrocarbons, *J. Atmos. Chem.*, 26, 189–222, 1997.
- Hu, D., Bian, Q., Li, T. W. Y., Lau, A. K. H., and Yu, J. Z.: Contributions of isoprene, monoterpenes,  $\beta$ -caryophyllene, and toluene to secondary organic aerosol in Hong Kong during the summer of 2006, *J. Geophys. Res.*, 113, D22206, doi:10.1029/2008JD010437, 2008.
- Iinuma, Y., Müller, C., Berndt, T., Claeys, M., and Herrmann, H.: Evidence for organosulfates in secondary organic aerosol from  $\beta$ -pinene ozonolysis and ambient aerosol, *Environ. Sci. Technol.*, 41, 6678–6683, 2007.
- Ion, A. C., Vermeylen, R., Kourtchev, I., Cafmeyer, J., Chi, X., Gelencsér, A., Maenhaut, W., and Claeys, M.: Polar organic compounds in rural PM<sub>2.5</sub> aerosols from K-pusztá, Hungary, during a 2003 summer field campaign: Sources and diel variations, *Atmos. Chem. Phys.*, 5, 1805–1814, 2005, <http://www.atmos-chem-phys.net/5/1805/2005/>.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5, 1053–1123, 2005, <http://www.atmos-chem-phys.net/5/1053/2005/>.
- Kavouras, I. G., Mihalopolous, N., and Stephanou, E. G.: Formation and gas/particle partitioning of monoterpenes photo oxidation products over forests, *Geophys. Res. Lett.*, 26, 55–58, 1999a.
- Kavouras, I. G., Mihalopoulos, N., and Stephanou, E. G.: Secondary aerosol formation vs. primary organic aerosol emission: in situ evidence for the chemical coupling between monoterpene acidic photooxidation products and new particle formation over forests, *Environ. Sci. Technol.*, 33, 1028–1037, 1999b.
- Kawamura, K. and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, 27, 2227–2235, 1993.
- Kleindienst, T., Jaoui, M., Lewandowski, M., Offenberg, J., Lewis, C., Bhave, P., and Edney, E.: Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location, *Atmos. Environ.* 41, 8288–8300, 2007.
- Klinger, L. F., Li, Q. J., Guenther, A. B., Greenberg, J. P., Baker, B., and Bai, J. H.: Assessment of volatile organic compound emissions from ecosystem of China, *J. Geophys. Res.*, 107(D21), 4603, doi:10.1029/2001JD001076, 2002.
- Kourtchev, I., Ruuskanen, T., Maenhaut, W., Kulmala, M., and Claeys, M.: Observation of 2-methyltetrols and related photooxidation products of isoprene in boreal forest aerosols from Hyytiälä, Finland, *Atmos. Chem. Phys.*, 5, 2761–2770, 2005, <http://www.atmos-chem-phys.net/5/2761/2005/>.
- Kourtchev, I., Warnke, J., Maenhaut, W., Hoffmann, T., and Claeys, M.: Polar organic marker compounds in PM<sub>2.5</sub> aerosol from a mixed forest site in western Germany, *Chemosphere*, 1308–1314, 2008a.
- Kourtchev, I., Ruuskanen, T., Keronen, P., Sogacheva, L., Reissell, A., Chi, X., Vermeylen, R., Kulmala, M., Maenhaut, W., and Claeys, M.: Determination of isoprene and  $\alpha$ - $\beta$ -pinene oxidation products in boreal forest aerosols from Hyytiälä, Finland: Diurnal variations and possible link with particle formation events, *Plant Biol.*, 10, 138–149, 2008b.
- Lewandowski, M., Jaoui, M., Kleindienst, T. E., Offenberg, J. H., and Edney, E. O.: Composition of PM<sub>2.5</sub> during the summer of 2003 in Research Triangle Park, North Carolina, *Atmos. Environ.*, 41, 4073–4083, 2007.
- Lewis, D. H. and Smith, D. C.: Sugar alcohols (polyols) in fungi and green plants. I. Distribution, physiology and metabolism, New

- Phytol., 66, 143–184, 1967.
- Ng, N. L., Kwan, A. J., Surratt, J. D., Chan, A. W. H., Chhabra, P. S., Sorooshian, A., Pye, H. O. T., Crounse, J. D., Wennberg, P. O., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO<sub>3</sub>), *Atmos. Chem. Phys.*, 8, 4117–4140, 2008, <http://www.atmos-chem-phys.net/8/4117/2008/>.
- Pacini, E.: From anther and pollen ripening to pollen presentation, *Plant. Syst. Evol.*, 222, 19–43, 2000.
- Plewka, A., Gnauk, T., Brüggeman, E., and Herrmann, H.: Biogenic contributions to the chemical composition of airborne particles in a coniferous forest in Germany, *Atmos. Environ.*, 40, S103–S115, 2006.
- Schkolnik, G., Falkovich, A. H., Rudich, Y., Maenhaut, W., and Artaxo, P.: New analytical method for the determination of levoglucosan, polyhydroxy compounds, and 2-methylerythritol and its application to smoke and rainwater samples, *Environ. Sci. Technol.*, 39, 2744–2752, 2005.
- Sharkey, T. D., and Yeh, S.: Isoprene emission from plants. *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, 52, 407–436, 2001.
- Simoneit, B. R. T.: Biomass burning – a review of organic tracers for smoke from incomplete combustion, *Appl. Geochem.*, 17, 129–162, 2002.
- Surratt, J. D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., Seinfeld, J. H.: Chemical composition of secondary organic aerosol formed the photooxidation of isoprene, *J. Phys. Chem. A.*, 110, 9665–9690, 2006.
- Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, *Environ. Sci. Technol.*, 41, 517–527, 2007a.
- Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J. H.: Effect of acidity on secondary organic aerosol formation from isoprene, *Environ. Sci. Technol.*, 41, 5363–5369, 2007b.
- Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, *J. Phys. Chem. A.*, 112, 8345–8378, 2008.
- Szmigielski, R., Surratt, J. D., Gómez-González, Y., Van der Veken, P., Kourtchev, I., Vermeylen, R., Blockhuys, F., Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Edney, E. O., Seinfeld, J. H., Maenhaut, W., and Claeys, M.: 3-methyl-1,2,3-butanetricarboxylic acid: An atmospheric tracer for terpene secondary organic aerosol, *Geophys. Res. Lett.*, 34, L24811, doi:10.1029/2007GL031338, 2007.
- Wang, G., Kawamura, K., Hatakeyama, S., Takami, A., Li, H., and Wang, W.: Aircraft measurement of organic aerosols over China, *Environ. Sci. Technol.*, 41, 3115–3120, 2007.
- Wang, G. and Kawamura, K.: Molecular characteristics of urban organic aerosols from Nanjing: A case study of a mega-city in China, *Environ. Sci. Technol.*, 39, 7430–7438, 2005.
- Wang, W., Vas, G., Dommissie, R., Loones, K., and Claeys, M.: Fragmentation study of diastereoisomeric 2-methyltetrols, oxidation products of isoprene, as their trimethylsilyl ethers using gas chromatography/ion trap mass spectrometry, *Rapid Commun. Mass Spectrom.*, 18, 1787–1797, 2004.
- Wang, W., Kourtchev, I., Graham, B., Cafmeyer, J., Maenhaut, W., and Claeys, M.: Characterization of oxygenated derivatives of isoprene related to 2-methyltetrols in Amazonian aerosols using trimethylsilylation and gas chromatography/ion trap mass spectrometry, *Rapid Commun. Mass Spectrom.*, 19, 1343–1351, 2005.
- Xia, X. and Hopke, P. K.: Seasonal variation of 2-methyltetrols in ambient air samples, *Environ. Sci. Technol.*, 40, 6934–6937, 2006.
- Yan, Y., Wang, Z., Bai, Y., Xie, S., and Shao, M.: Establishment of vegetation VOC emission inventory in China, *China Environ. Sci.*, 25, 110–114, 2005.
- Yu, L. E., Shulman, M. L., Kopperud, R., and Hildemann, L. M.: Characterization of organic compounds collected during the southeastern aerosol and visibility study: water-soluble organic species, *Environ. Sci. Technol.*, 39, 707–715, 2005.