Contributions of Isoprene, Monoterpenes, β -Caryophyllene, and Toluene to Secondary Organic Aerosols in Hong Kong during the Summer of 2006

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Abstract

Isoprene, monoterpenes, β -caryophyllene, and toluene are known to be important secondary organic aerosol (SOA) precursors. In this study, characteristic SOA tracers of these precursors were quantified in ambient samples of PM_{2.5} taken in Hong Kong and their contributions to SOA were estimated using a tracer-based method. Samples were collected every other day from four sampling sites during a field measurement campaign in the summer of 2006. Fourteen SOA tracers, along with twenty-four other polar oxygenated compounds, were identified and quantified using gas chromatography/ion trap mass spectrometry with prior trimethylsilylation. Concentrations of the individual tracers ranged from a few tenths to a few hundreds ng m⁻³. The tracer concentrations were found to be one order of magnitude higher on days under regional transport influences due to elevated oxidant levels than on days under mainly local emissions influences. Using the measured SOA tracer concentrations in the ambient aerosols and laboratory-derived tracer mass fractions reported by *Kleindienst et al.* [2007], we estimated that the average SOA attributable to isoprene, monoterpenes, β -caryophyllene, and toluene was 8.83 $\mu\text{g m}^{-3}$ on days under regional transport influences versus 0.99 $\mu\text{g m}^{-3}$ on days under mainly local emissions influences, accounting for approximately 45% and 14%, respectively, of the ambient OC concentrations. The tracer-based estimates indicate that monoterpenes and β -caryophyllene are significant contributors to ambient PM_{2.5} in the summer, which may be due to the high emissions of

28 these biogenic hydrocarbons in Hong Kong.

29 **Keywords: SOA; Organic tracers; SOC contributions; SOA contributions; Biogenic**
30 **hydrocarbons; Anthropogenic hydrocarbons**

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32 **1. Introduction**

33 Secondary organic aerosols (SOA) formed from atmospheric reactions of volatile organic
34 compounds (VOCs) contribute 50% to 90% of the organic carbon in fine urban and regional
35 particles on smoggy or summer days [Turpin and Huntzicker, 1995; Lim and Turpin, 2002;
36 Schauer *et al.*, 2002]. Terpene emissions from vegetation, together with aromatic
37 hydrocarbons from anthropogenic sources, have long been recognized as important
38 precursors of SOA [Went, 1960; Anderson-Skold and Simpson, 2001; Kalberer *et al.*, 2004;
39 Odum *et al.*, 1997]. Although our understanding of aerosol (especially SOA) formation has
40 been greatly advanced in the last decade, complete molecular-level chemical characterization
41 of the organic mixtures in PM_{2.5} still remains unachieved. In the past five years, many efforts
42 have been expended on the identification of SOA tracers. SOA tracers of isoprene,
43 monoterpenes, β -caryophyllene, and toluene were characterized in smog chamber
44 experiments and detected in ambient samples [Claeys *et al.*, 2004a; Claeys *et al.*, 2007; Jaoui
45 *et al.*, 2005; Jaoui *et al.*, 2007; Kleindienst *et al.*, 2004; Szmigielski *et al.*, 2007]. Building
46 upon the progress in identifying tracer compounds specific to certain precursors, Kleindienst
47 *et al.* [2007] recently developed a tracer-based approach to estimate the contributions of
48 individual biogenic and anthropogenic hydrocarbons to ambient organic carbon (OC)
49 concentrations in PM_{2.5}. In this approach, the mass fractions of tracer compounds in SOA
50 derived from smog chamber studies and the SOA tracer concentrations measured in ambient
51 PM_{2.5} were used to derive the estimates of contributions by individual precursors to SOA.
52 Although this tracer-based method needs further assessment in terms of the selection of tracer

53 compounds and is subject to considerable uncertainty due to the simplification in using the
54 laboratory-derived, single-valued tracer mass fractions to estimate the secondary organic
55 carbon (SOC) contribution, a comparison between the SOA tracer method and ^{14}C
56 measurements suggests that this tracer-based method provides preliminary estimates of the
57 SOC contributions by individual hydrocarbon precursors and is useful in identifying major
58 SOA precursors without an accurate and complete understanding of the molecular
59 composition of SOA [Offenberg *et al.*, 2007]. This in turn facilitates the development of
60 cost-effective air pollution control strategies for aerosols.

61 In this study, fifty-one $\text{PM}_{2.5}$ samples collected from four sites in Hong Kong during the
62 summer of 2006 were analyzed by a derivatization technique combined with gas
63 chromatography-ion trap mass spectrometric (GC/ITMS) analysis. SOA tracer compounds
64 formed from atmospheric oxidation of isoprene, monoterpenes, β -caryophyllene and toluene
65 were quantified and used to estimate SOC and SOA contributions of these hydrocarbon
66 precursors to ambient OC and organic matter (OM). As far as we are aware, this is the first
67 time that the SOA tracers were identified in field samples collected in Asia and used to
68 estimate the contributions of individual precursors to SOA and SOC. Our work adds to the
69 increasing database on the chemical characteristics of ambient SOA.

70

71 **2. Experimental Method**

72 **2.1 Site description and aerosol sampling**

73 The aerosol samples were collected every other day from four sites in Hong Kong ($114^{\circ}15'$ E,
74 $22^{\circ}13'$ N), including Yuen Long (YL), Tsuen Wan (TW), Tung Chung (TC) and the Hong
75 Kong University of Science and Technology (HKUST) (Figure 1). Of the four sampling sites,
76 YL and TW are urban sites in densely populated residential areas, TC is a less-populated
77 residential new town close to the airport, and HKUST is a sub-urban site with the nearest

commercial center more than 5 km away. Although Hong Kong is a highly urbanized city, 38% (416 km²) of the Hong Kong land area is designated as country parks and special areas, which are mainly covered by vegetation [Hong Kong Agriculture, Fisheries and Conservation Department, 2007]. There are more than 3164 native and introduced vegetation species in Hong Kong and the major vegetation belongs to the evergreen broad-leaved forest of the subtropics [Hong Kong Herbarium, 2004]. Tree distribution estimation based on field survey data between 2004 and 2006 showed that ten tree species belonging to the families of Theaceae, Myrtaceae, Lauraceae, Clusiaceae, Araliaceae and Mimosaceae contributed 76% of the total biogenic VOC emissions in Hong Kong [Tsui *et al.*, 2008].

A total of 51 samples were collected between 8 July and 3 August 2006 as part of an air quality characterization campaign in the Pearl River Delta (PRD). Sampling started at 7 am and lasted for 24 h. The aerosol samples were collected on 20 cm × 25 cm quartz fiber filters (QMA, Whatman, Clifton, NJ) using a high volume (Hi-Vol) PM_{2.5} sampler (Graseby-Andersen, Atlanta, GA) operated at a flow rate of 1130 L min⁻¹. The quartz-fiber filters were baked before sampling at 550°C for 12 h to remove organic contaminants. In parallel with the Hi-Vol sampler, an R&P Partisol sampler (model 2000, Rupprecht and Patashnick, Albany, NY) with a 2.5 µm inlet was used to collect PM_{2.5} on 47-mm Teflon membrane filters (Pall Life Sciences, Ann Arbor, MI) at a flow rate of 16.7 L min⁻¹. Each Teflon filter was weighed before and after the sample collection for determination of PM_{2.5} mass concentrations. Quartz and Teflon filter field blanks were also collected at each site. All filter samples were transferred back to our laboratory in a cooler and stored at -18°C in a refrigerator before analysis.

2.3 Analysis of elemental and organic carbon

A 1×1 cm² punch was removed from each quartz fiber filter and analyzed for elemental carbon (EC) and organic carbon (OC) using a thermal/optical transmittance aerosol carbon

analyzer (Sunset Laboratory, Oregon, USA) [Birch and Cary, 1996]. The analysis started in a non-oxidizing atmosphere (helium), purged for 10 s followed by four temperature steps at 340, 500, 615, 870°C for 60, 60, 60, and 90 s, respectively. The oven was then briefly cooled for 10 s before the gas valve was switched to 2% O₂/98% He, followed by five steps of heating at 550, 625, 700, 775, and 850°C [Schauer et al., 2003].

2.4 Chemical analysis

Polar organic compounds bearing hydroxyl and carboxylic groups were identified and quantified by the N,O-bis-(trimethylsilyl) trifluoroacetamide [BSTFA, with 1% trimethylchlorosilane] derivatization technique combined with GC/ITMS analysis. Twenty punches of 1×1.45 cm² sized pieces were removed from each quartz filter and extracted and derivatized for GC/MS analysis. Prior to extraction, the filter pieces were spiked with 20 µl of chrysene-*d*₁₂ (214 µg ml⁻¹ in *n*-hexane) as the internal standard. The filters were sonicated three times for 10 min each in 15 mL of HPLC-grade methanol. The extract was filtered through a Millipore 0.2-µm PTFE hydrophobic Teflon filter, transferred into a 50 ml round flask and concentrated to ~1 mL by rotary evaporation. The extract was then transferred to a 5 ml reaction vial. Residues remaining on the wall of the round flask were rinsed with ~2 ml of dichloromethane and combined with the extract. The extract was then blown to dryness at 40°C under a gentle stream of ultra-pure nitrogen and derivatized with 100 µl BSTFA and 50 µl pyridine at 70°C for 2 h. After the solution cooled down to room temperature, 30 µl of tetracosane-*d*₅₀ (50 µg ml⁻¹ in *n*-hexane) was added. The resulting trimethylsilyl derivatives were analyzed by a Varian 3800 gas chromatograph interfaced to a Saturn 2000 Ion Trap MS (Varian, Inc. Palo Alto, CA) operated in the electron ionization (EI) mode. An aliquot of 2 µL of the derivatized sample (or standard mixtures) was injected. Separation was carried out on an AT-5ms column (30m×0.25 mm×0.25 µm, Alltech). The GC oven was initially held at 80°C for 5 min, heated at 3°C min⁻¹ to 200°C, held for 2 min, then increased to 300°C at 15°C

min⁻¹, and held at 300°C for 25 min. Temperatures of the injector, the ion trap and the interface were set to 275, 200, and 300°C, respectively.

Calibration curves were constructed in appropriate concentration ranges by derivatizing and analyzing a series of commercially available compounds. All the compounds were used as received without further purification. Saccharides and dicarboxylic acids, where the authentic standards were available, were identified and quantified by direct comparison to the standards. The SOA tracer compounds do not have available pure reference compounds. They were identified by comparing their mass spectra with the previously reported data [Claeys *et al.*, 2004a; Claeys *et al.*, 2007; Jaoui *et al.*, 2007; Kleindienst *et al.*, 2007; Szmigielski *et al.*, 2007] and their retention times relative to other known compounds in the GC chromatograms. Some of the samples were also analyzed in the chemical ionization mode to ensure correct peak identification. Their concentrations were estimated by using the response factors of surrogate compounds with similar structures and functional groups. The surrogate compounds are specified in the footnotes to Table 3. It should be noted that Kleindienst *et al.* [2007] derived mass fractions of SOA tracers by using ketopinic acid as the surrogate for all tracer compounds; while different surrogates were used in this study. The quantification uncertainty caused by using surrogate calibration and different surrogates other than ketopinic acid was estimated to be within a factor of 3.

Recoveries of the target compounds were obtained by spiking standards onto pre-baked blank quartz filters, followed by extracting and analyzing them in the same way as with the collected samples. Recoveries for saccharides were in the range of 71-112%, with the highest recovery for α - and β -fructose and the lowest recovery for α - and β -xylose. Recoveries of hydroxyl dicarboxylic acids were the lowest of all the acids, with 52% for citramalic acid and 59% for malic acid. Recoveries of the other dicarboxylic acids ranged from 73% to 114%.

3. Results and discussion

3.1 Meteorology and air quality data

Hourly meteorological and air quality data (i.e., temperature, relative humidity (RH), ozone, and SO₂ concentrations) at YL, TW, and TC were measured by the Hong Kong Environmental Protection Department (HKEPD) and the Hong Kong Observatory. The average temperature and relative humidity (RH) data, average ozone and SO₂ concentrations and their peak hourly concentrations are reported in Table 1 for the YL site. Meteorology and air quality data for the other three sites are given in the supplementary material. During the sampling period, the ambient temperature ranged from 23.2 to 37.8°C, with an average daily temperature of 29.5°C. The daily average RH ranged from 59 to 90%. Heavy rainstorms occurred on 8, 9, 16, 27, 28 and 29 July and 3 August. The daily precipitation amounts at the HKUST site on these days were 35, 37, 136, 50, 89, 87 and 82 mm respectively. Similar amounts of precipitation were observed at the YL (Table 1) and TC sites on these days (no precipitation data was available for the TW site). Heavy rainstorms during summer are common in Hong Kong, where the climate is under the influence of the Asian monsoon.

Hong Kong is a highly urbanized coastal city. The pollution sources of ambient PM_{2.5} in Hong Kong are influenced by land-sea breezes, the mountainous topography, the urban street canyon effect, and the complex monsoon meteorology. Hong Kong is located at the southeast edge of the rapidly developing PRD, the northern part of which is identified to be a major source area influencing PRD regional air pollutant concentrations [Hagler *et al.*, 2006]. Under conditions favoring land-sea breeze circulations, pollutants emitted in the other parts of the PRD are brought into Hong Kong, significantly elevating air pollutant concentrations in Hong Kong [Louie *et al.*, 2005; Lo *et al.*, 2006].

Lau *et al.* [2007] used SO₂ as the tracer to examine the origin of air pollution sources in

Hong Kong on each day of 2006. The weather conditions and spatial pollution pattern of SO₂ were assessed daily to identify the most dominant pollution source (i.e., local versus regional). Using Lau et al.'s results as a reference, we carefully inspected the formation trend of SOA, PM_{2.5} and ozone in this study and identified that four days during the entire sampling period, i.e., 14, 24 and 26 July and 1 August, were mainly affected by regional sources (Table 1). On these days, the land-sea breeze circulations brought the pollutants emitted in the PRD region into Hong Kong, leading to higher ambient PM_{2.5} and oxidant concentrations. The 36-h back trajectories (Figure S1) also confirm air masses traveled over the PRD region before arriving at Hong Kong on these days. On the remaining ten sampling days, the prevailing winds were southeasterly or southwesterly. As a result, the air quality was mainly influenced by local sources. On these days, low to moderate SO₂, O₃ and PM_{2.5} levels were observed. For ease of the ensuing discussions, we hereafter call the days influenced by regional aerosol sources “the regional days” and the days mainly influenced by local emissions “the local days”. The classification of local and regional days for individual sampling days is given in Table 1.

3.2 Concentrations of PM_{2.5} mass, EC and OC

The average concentrations of PM_{2.5} mass, EC, and OC at the four sampling locations during the sampling period influenced by local versus regional sources are summarized in Table 2. PM_{2.5} mass, EC and OC data for individual samples from the YL site are listed in Table 1. Information for the other three sites is given in the supplementary material. The ambient PM_{2.5} mass concentrations ranged from 2.72 to 90.7 µg m⁻³. EC and OC concentrations ranged from 0.20 to 5.00 µgC m⁻³ and 0.61 to 22.3 µgC m⁻³, respectively. There were stark contrasts in concentrations of PM_{2.5} mass and the constituent species between the regional days and the local days. As shown in Table 2, the average PM_{2.5} mass and OC concentrations on the regional days were more than three times higher than those on the local days. The EC concentrations under these two synoptic conditions were similar

during the whole sampling period, consistent with the general consensus that EC is dominated by local emissions in Hong Kong [Yu *et al.*, 2004; Yuan *et al.*, 2006]. If the factor of 1.9 was used to estimate OM in the samples under local emissions influences and 2.2 in samples with influences from regional sources, OM was estimated to account for 44% of PM_{2.5} mass on average. The OM-to-OC ratios for aerosols collected in Hong Kong were measured previously in our group by coupling thermal gravimetric and chemical analyses [Chen and Yu, 2007]. An OM/OC ratio of 2.2 was applicable to aerosols dominated by continent-originated air mass, and 1.9 was applicable to aerosols dominated by marine air mass.

3.3 Characterization of secondary organic tracer compounds and other polar oxygenated compounds

A representative GC/MS total ion chromatogram (TIC) for a BSTFA-derivatized sample is presented in Figure 2. Thirty eight polar oxygenated organic compounds were identified and quantified, including 14 SOA tracer compounds, 14 saccharides, 8 dicarboxylic acids and 2 fatty acids. All compounds were identified by comparing their EI mass spectra with those of authentic standards or previously reported mass spectral data [Claeys *et al.*, 2004a; Claeys *et al.*, 2007; Jaoui *et al.*, 2007; Kleindienst *et al.*, 2007; Szmigielski *et al.*, 2007]. The chemical names of these identified compounds and their mass concentrations in the samples collected at YL are listed in Table 3. Data for the other three sites are provided in the supplementary material.

Six compounds previously identified to be isoprene SOA tracers were detected in our samples, including 2-methylglyceric acid (peak 4 in Fig. 2), three C₅ alkene triols (peaks 5, 6, 7), and two 2-methyltetrols (peaks 14 and 15) (Table 3). The 2-methyltetrols were first observed in the ambient PM_{2.5} aerosols collected from the Amazonian rainforest [Claeys *et al.*, 2004a] and subsequently used as the tracer compounds for isoprene photo-oxidation in the

atmosphere [Kourtchev *et al.*, 2005; Edney *et al.*, 2005; Surratt *et al.*, 2006]. In this study, concentrations of 2-methyltetrols were estimated to range from 0.44 to 73.1 ng m⁻³. The C₅ alkene triols were postulated to be formed from the intermediate epoxydiol derivatives of isoprene through acid-catalyzed reactions [Wang *et al.*, 2005], and were first detected in laboratory-generated SOA formed from the photo-oxidation of isoprene under low-NO_x (or NO_x free) conditions [Surratt *et al.*, 2006]. On most sampling days, C₅ alkene triols were found to have higher concentrations than the 2-methyltetrols had. The summed concentrations of the C₅ alkene triols were normally less than 50 ng m⁻³, but could be as high as 426 ng m⁻³ on regional days. 2-Methylglyceric acid was possibly formed from the further oxidation of methacrolein and methacrylic acid, two major gas-phase oxidation products of isoprene [Claeys *et al.*, 2004b; Edney *et al.*, 2005; Surratt *et al.*, 2006].

Six compounds previously identified to be tracers for SOA formed from monoterpenes [Jaoui *et al.*, 2005; Claeys *et al.*, 2007] were detected in our samples (Peaks 19, 16, 28, 26, 18 and 25 in Figure 2). They are two hydroxydicarboxylic acids (namely 3-hydroxyglutaric acid and 3-hydroxy-4,4-dimethylglutaric acid), one C₈-tricarboxylic acid (i.e. 3-methyl-1,2,3-butanetricarboxylic acid), and three alkyl- or acetyl-substituted dicarboxylic acids (i.e., 3-isopropyl pentanedioic acid, 3-acetyl pentanedioic acid and 3-acetyl hexanedioic acid). The C₈-tricarboxylic acid and the two hydroxydicarboxylic acids were recently identified in the ambient fine aerosols collected at K-pusztá and were proposed to be the SOA tracer compounds for the photo-oxidation of α -pinene [Szmigielski *et al.*, 2007; Claeys *et al.*, 2007]. The C₈-tricarboxylic acid was previously tentatively identified as 3-carboxyheptanoic acid [Jaoui *et al.*, 2005] and 2-hydroxy-4-isopropyladipic acid based on the EI mass spectra of a synthesized isomeric reference compound [Claeys *et al.*, 2007]. However, most recently, Szmigielski *et al.* [2007] confirmed its structure as 3-methyl-1,2,3-butanetricarboxylic acid by comparing its gas and liquid chromatographic behaviors and mass spectral characteristics

with those of a synthesized reference compound. Laboratory studies showed that besides α -pinene, other monoterpenes (e.g., β -pinene and d-limonene) also serve as the precursors of 3-isopropyl pentanedioic acid, 3-acetyl pentanedioic acid, 3-acetyl hexanedioic acid and 3-methyl-1,2,3-butanetricarboxylic acid [Jaoui *et al.*, 2005; Szmigielski *et al.*, 2007]. Like the C_5 alkene triols, both 3-hydroxyglutaric acid and the C_8 -tricarboxylic acid showed noticeably higher concentrations on the days influenced by regional sources, which were up to the level of 417 and 477 ng m⁻³, respectively. The total estimated concentrations of the six monoterpene SOA tracers ranged from 8 to 1115 ng m⁻³.

The monoterpene SOA, when compared with isoprene SOA, was a more significant component of ambient OM in Hong Kong during the summer of 2006. *cis*-Pinic acid and *cis*-pinonic acid, two major photo-oxidation products of α -pinene observed in smog chamber experiments [Jang and Kamens, 1998; Yu *et al.*, 1999], were not detected in our aerosol samples. They were found at a trace level (normally less than 2 ng m⁻³) or undetectable in aerosol samples collected at five Midwestern US cities during July and August 2004 [Lewandowski *et al.*, 2008]. However, we detected in all our samples 3-methyl-1,2,3-butanetricarboxylic acid, the C_8 -tricarboxylic acid proposed to be a multi-generational oxidation product of *cis*-pinonic acid in the presence of NO_x and to be formed at the expense of *cis*-pinic acid [Szmigielski *et al.*, 2007]. During the sampling periods the temperature and gas phase oxidant concentrations (such as ozone, NO_x and SO₂, especially on the days influenced by regional emissions) were high, which favored the fast photo-oxidation of and aerosol formation from α -pinene [Claeys *et al.*, 2007]. The detection of 3-methyl-1,2,3-butanetricarboxylic acid in the ambient aerosols implies fairly complete and fast oxidation of α -pinene in the atmosphere and also explains the absence of *cis*-pinic acid and *cis*-pinonic acid in our aerosol samples.

β -Caryophyllinic acid, a tracer for β -caryophyllene SOA formation, was identified in all

the samples (Peak 37 in Figure 2). β -Caryophyllinic acid can be formed either by ozonolysis of β -caryophyllene or through photo-oxidation of β -caryophyllene [Jaoui *et al.*, 2003; Jaoui *et al.*, 2007]. The estimated concentrations of β -caryophyllinic acid in our samples were generally less than 10 ng m^{-3} , but could be up to 80 ng m^{-3} on the regional days.

The 2,3-dihydroxy-4-oxopentanoic acid was proposed to be a tracer compound for toluene SOA. It was first observed by Kleindienst *et al.* [2004] in SOA generated from toluene/ NO_x smog chamber experiments and in ambient fine aerosols collected in Philadelphia, PA, USA during the summer of 2001. Since no mass spectrum of TMS-derivatized 2,3-dihydroxy-4-oxopentanoic acid is available, its reported major ions in EI mode and relative retention time in the GC chromatogram [Kleindienst *et al.*, 2007] were used to identify peak 11 in Figure 2 tentatively as 2,3-dihydroxy-4-oxopentanoic acid in this study. The EI mass spectrum of the TMS derivatized 2,3-dihydroxy-4-oxopentanoic acid obtained in this study is shown in Figure S2. Double derivatization with O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) and BSTFA was also used with some ambient samples to confirm the presence of 2,3-dihydroxy-4-oxopentanoic acid. This tracer compound was generally found at a level of less than 1 ng m^{-3} in most samples and it co-eluted with adipic acid, which made its detection in the ambient samples difficult.

In addition to the SOA tracer compounds, we have also identified and quantified a group of fourteen saccharides, eight dicarboxylic acids ($>\text{C}_3$), and two fatty acids (i.e., C_{16} and C_{18} alkanolic acids, which are often used as marker compounds for cooking emissions [Robinson *et al.*, 2006]) (Table 3). Among the saccharides quantified in the present study, the major ones were levoglucosan, α - and β -xylose, α - and β -glucose, α - and β -fructose and meso-erythritol. For saccharides with α - and β - isomers, the two isomers were added together for concentration data. Levoglucosan (peak 22), a key tracer for biomass burning aerosols, was the most abundant saccharide species, with concentrations ranging from 1.67 to 97.7 ng

m⁻³. This level is comparable to that reported by *Wan and Yu* [2007] in the ambient samples collected in August 2004 at HKUST.

Among the quantified dicarboxylic acids, malic acid (2-hydroxy-butanedioic acid) was the most abundant, with an average concentration of 192 ng m⁻³ and up to 662 ng m⁻³ on the regional days. A number of recent studies have reported concentrations of malic acid up to 194 ng m⁻³ in a rural area of Germany in the summer [*Rohrl and Lammel*, 2002] and an average of 59 ng m⁻³ in Beijing, China [*Huang et al.*, 2005]. Because of its structure similarity with succinic acid, malic acid was proposed to be a photo-oxidation product of succinic acid and succinic acid was thought to be among late products in the atmospheric oxidation of unsaturated fatty acids [*Kawamura and Ikushima*, 1993; *Kawamura et al.*, 1996]. More recently, *Claeys et al.* [2004] suggested that malic acid might be produced by oxidation of other biogenic VOCs besides unsaturated fatty acids. Our data show that malic acid was highly correlated with 3-hydroxyglutaric acid ($r^2=0.70$, $n = 51$), one of the monoterpene SOA tracers, supporting the suggestion of biogenic VOCs as significant precursors for malic acid. The presence of malic acid increased by 3.8-5.2 times on the regional days than on the local days at the four sampling sites, consistent with its secondary origin.

Citramalic acid (2-hydroxy-2-methyl-butanedioic acid) is structurally similar to malic acid and was present in all samples at levels one magnitude lower than that of malic acid. This compound also showed a large concentration contrast between regional and local samples. Its average concentration in the regional samples (19.8 ng m⁻³) was more than five times that in the local samples (3.4 ng m⁻³). *Lewandowski et al.* [2007] also identified this compound at a similar concentration level (5-55 ng m⁻³) in Research Triangle Park, NC, USA. Concentrations of citramalic acid were found to have a good correlation with those of malic acid ($r^2=0.75$, $n = 51$) in this study, indicating that the two hydroxydicarboxylic acid compounds likely have common precursor sources and formation pathways.

Hexadecanoic acid and octadecanoic acid (peaks 39 and 40 in Figure 2) were also quantified in the samples. Cooking emissions are known to be a major source of these two fatty acids in urban areas. Their concentrations varied from 6.87 to 17.6 ng m⁻³ and 2.61 to 8.68 ng m⁻³, respectively. In contrast to the SOA tracers, these two fatty acids had similar concentrations on the regional and the local days, with the concentration ratios of 0.9-1.2 between samples collected on days under two types of synoptic weather conditions. The comparable concentrations on regional and local days suggested that their major sources were local.

3.4 Estimates of ambient SOC and SOA contributions

A tracer-based method, first proposed by *Kleindienst et al.* [2007], was used to assess the SOC and SOA contributions of monoterpenes, isoprene, β -caryophyllene and toluene to ambient OC and OM. By using the smog chamber experimental data of different hydrocarbon/NO_x mixtures, *Kleindienst et al.* [2007] derived the mass fraction of tracer compounds in SOA (f_{soa}) generated from individual precursor, which was defined as

$$f_{soa, hc} = \frac{\sum_i [tr_i]}{[SOA]}, \quad (1)$$

where $\sum_i [tr_i]$ is the sum of the concentrations of the selected suite of tracers for a same VOC precursor in $\mu\text{g m}^{-3}$, and $[SOA]$ is the measured SOA concentration in $\mu\text{g m}^{-3}$ in chamber studies. The laboratory-derived f_{soa} for α -pinene, isoprene, β -caryophyllene and toluene were 0.168 ± 0.081 , 0.063 ± 0.016 , 0.0109 ± 0.0022 , and 0.0040 ± 0.0013 , respectively. Carbon mass fractions of the tracer compounds in the laboratory-generated SOC (f_{soc}) from these four hydrocarbon precursors were determined as well, which were 0.231 ± 0.111 , 0.155 ± 0.111 , 0.0230 ± 0.0046 , and 0.0079 ± 0.0026 , respectively.

The same sets of tracers as those listed in the study by *Kleindienst et al.* [2007] were used for SOA estimation. Since no pinic acid, pinonic acid or

3-(2-hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid was found in the samples, the five multifunctional dicarboxylic acids and the C₈-tricarboxylic acid were used as the tracer compounds for SOA attributable to α -pinene. Three of the α -pinene SOA tracer compounds were also identified in the smog chamber-generated SOA of β -pinene and d-limonene [Jaoui et al., 2005]. It is therefore reasonable to attribute the estimated contributions of α -pinene to SOC and SOA to monoterpenes. Using the tracer compound concentrations determined in the ambient aerosols for this work and the laboratory-derived f_{soa} and f_{soc} values by Kleindienst et al., we then estimated the SOA and SOC contributions of monoterpenes, isoprene, β -caryophyllene and toluene to ambient OM and OC (Figure 3, only showing SOC contributions). The individual SOC and SOA contributions attributable to the hydrocarbon precursors are tabulated in Table 2 for individual samples collected at the YL site. The mass percentages of the total estimated SOC and SOA in ambient OC and OM are also presented in Table 2.

There was a stark difference in the amounts of SOA and the relative contributions of SOA to OM between the regional and the local days. The average SOA amount generated on the regional days was about nine times that on the local days (Table 2). We therefore separately discuss SOA contributions on the regional and the local days.

As discussed earlier in Section 3.1, significantly elevated levels of air pollutants were observed in Hong Kong on the regional days. The higher oxidant concentrations (such as NO_x, O₃ and SO₂) transported from the northern part of the PRD led to more rapid atmospheric oxidation and secondary aerosol formation from VOC precursors. Therefore, as shown in Figure 3, higher OC concentrations, as well as higher SOC contributions, were observed on the regional days. The average SOA attributable to isoprene, monoterpenes, β -caryophyllene, and toluene was estimated to be 8.83 $\mu\text{g m}^{-3}$ on regional days versus 0.99 $\mu\text{g m}^{-3}$ on local days, accounting for approximately 45% and 14% of the ambient OC

concentrations, respectively (Table 2). Monoterpenes and β -caryophyllene were found to make much larger contributions to SOA on the regional days, which ranged from 0.75 to 6.63 $\mu\text{g m}^{-3}$ and 0.40 to 7.37 $\mu\text{g m}^{-3}$, respectively. Isoprene, which was found to be the largest SOA contributor among the same four precursors examined in the summer samples collected at Research Triangle Park, NC, USA [Kleindienst *et al.*, 2007], contributed 0.03 - 0.81 $\mu\text{gC m}^{-3}$ to SOC and 0.07- 1.99 $\mu\text{g m}^{-3}$ to SOA on the regional days. The contributions of toluene to SOC and SOA on the regional days were in the range of 0.25 - 0.82 $\mu\text{gC m}^{-3}$ and 0.49 - 1.61 $\mu\text{g m}^{-3}$, respectively.

The SOA mass contributions attributable to individual precursors on the local days were on average 5-14 times lower than those on the regional days. Moreover, unlike on the regional days when monoterpenes and β -caryophyllene were the most significant SOA contributors, almost the same amount of SOA was contributed by the four individual precursors on the local days. As shown in Table 1, lower O_3 and SO_2 concentrations were observed on the local days. Precipitation was observed on most local days as well. Since these SOA tracers normally have multiple hydroxyl and carboxylic groups, they could be easily washed out by rain due to their high water solubility. The less active formation but more removal through wet deposition of these SOA tracers may explain the low concentrations of these SOA tracers and the trivial differences between the SOA contributed by the different hydrocarbon precursors on the local days.

The averaged contribution of isoprene to SOC was 0.2 $\mu\text{gC m}^{-3}$ over the whole sampling period while the average isoprene contribution to SOC was 0.46 $\mu\text{gC m}^{-3}$ on the regional days and 0.09 $\mu\text{gC m}^{-3}$ on the local days (Table 2). The contribution of isoprene to SOC in our samples was about six times smaller than that estimated by Kleindienst *et al.* [2007] in their summer samples. The contributions of monoterpenes and β -caryophyllene to SOC were 0.9 and 0.61 $\mu\text{gC m}^{-3}$, respectively, about the same as those observed in USA. The difference in

the contribution of isoprene to SOC in Hong Kong and in southeastern USA was most probably due to the different vegetation coverage in the two locations. The observation of larger amounts of SOC and SOA masses attributable to monoterpenes rather than isoprene on the regional days is consistent with the considerably higher emissions of monoterpenes than of isoprene in Hong Kong, in addition to the higher SOA forming potential by monoterpenes. The annual emissions were estimated to be 3.5×10^9 g C yr⁻¹ for monoterpenes and 1.3×10^9 g C yr⁻¹ for isoprene [Tsui *et al.*, 2008]. Both isoprene and monoterpenes have the highest emissions in summer.

β -Caryophyllene was reported to constitute 66% of the sesquiterpene emissions in Research Triangle Park, NC USA and its emissions increased significantly with increasing ambient temperature [Helmig *et al.*, 2006]. It degrades rapidly in the atmosphere, with lifetimes of 2 min in the presence of 30 ppb O₃ and 53 min in the presence of 1.6×10^6 molecule cm⁻³ of OH radical [Shu and Atkinson, 1995]. β -Caryophyllene has a significant SOA formation potential. A model study of the Scandinavian atmosphere showed that β -caryophyllene, although only accounting for 2% of the total biogenic VOC emissions, contributed 12% to the total biogenic SOA formation [Anderson-Skold and Simpson, 2001]. β -Caryophyllinic acid was used as the SOA tracer for β -caryophyllene in this study. However, acidic isomers of β -caryophyllinic acid could be formed from the photo-oxidation of other sesquiterpenes having an endocyclic C=C bond, which might co-elute with β -caryophyllinic acid. Therefore, the estimated contribution of β -caryophyllene to SOA may represent a broader class of sesquiterpenes. The observation of significant SOC and SOA contributions of β -caryophyllene in this study ($1.58 \mu\text{gC m}^{-3}$ and $3.34 \mu\text{g m}^{-3}$ on the regional days, Table 2) suggests significant emissions of sesquiterpenes in Hong Kong during the summer. An emission inventory for sesquiterpenes in Hong Kong will be useful for a better understanding of SOA formation in the area.

The average contribution by toluene to SOC was $0.47 \mu\text{gC m}^{-3}$ on the regional days and $0.09 \mu\text{gC m}^{-3}$ on the local days, with an average of $0.21 \mu\text{gC m}^{-3}$ over the whole sampling period (Table 2). Smog chamber experiments by *Kleindienst et al* [2007] showed that the SOA tracer of toluene could also be formed from the photo-oxidation of xylenes. Therefore, the estimated contribution of toluene to SOA may to some extent represent a broader class of aromatics. Although the estimated SOA contributions of toluene were found to be considerably lower than the SOA contributions by the biogenic hydrocarbons examined in this study, this result does not necessarily imply that toluene is a less important SOA precursor in Hong Kong. As discussed earlier, the SOA tracer of toluene co-eluted with adipic acid in GC and was found at trace levels in most samples. Therefore, estimates of contribution of toluene to SOA were associated with high uncertainty due to the analytical difficulty in quantifying its tracer. We note that 2,3-dihydroxy-4-oxopentanoic acid was also found at a trace level (normally less than 2 ng m^{-3}) in aerosol samples collected in five Midwestern US cities by *Lewandowski et al.* [2008]. The generally low level of this tracer suggests that a more easily detectable toluene SOA tracer is needed for this tracer based method. The tracer-based approach did not consider SOA formed through in-cloud processing of small oxidation products (e.g., glyoxal, methylglyoxal). Recent modeling work [*Lim et al.*, 2005] suggested that glyoxal and methylglyoxal can partition into cloud droplets and yield SOA through the in-cloud formation of carboxylic acids (e.g., glyoxylic, glycolic and oxalic acids) and subsequent cloud evaporation. Since this in-cloud production was not represented in the laboratory-derived SOA mass fraction of toluene, SOA generated by the oxidation of toluene in the real atmosphere could be higher than what has been estimated here. Moreover, toluene is the only anthropogenic VOCs considered in this study due to the very limited information on SOA tracers and mass fractions available so far. Laboratory studies have shown considerable SOA yields from other aromatic compounds, such as xylenes,

ethylbenzene, ethyltoluenes, trimethylbenzene, and benzene [Odum *et al.*, 1997; Martin-Reviejo and Wirtz, 2005]. Ambient VOC measurements in Hong Kong indicated that the summed concentration of the above aromatic compounds were comparable to that of toluene during the summer [e.g., Guo *et al.*, 2007]. We currently lack SOA tracer compounds for these aromatic compounds. Clearly, more information on their SOA tracer selections and tracer mass fractions in SOA are needed for the estimation of their SOC and SOA contributions.

As discussed earlier, monoterpenes and β -caryophyllene are more significant SOA contributors than are isoprene and toluene during the entire sampling period. The percentage contributions to OC by monoterpenes and β -caryophyllene SOA on the regional days were two to three times higher than those on the local days. In comparison, the percentage contributions to OC by SOA of isoprene and toluene increased by less than 25% on the regional days compared with the local days. The lifetimes of β -caryophyllene, d-limonene, α -pinene, isoprene and toluene in 30 ppb of ozone at 298 K were 2, 119, 275, 1860, and 2.0×10^7 min, respectively [Shu and Atkinson, 1995; Atkinson, 1997; Calvert *et al.*, 2002]. A recent laboratory study found that terpenes with more than one double bond (such as β -caryophyllene, d-limonene and terpinolene) showed a different time-dependence SOA growth profile than that of the terpenes with a single double bond (such as α -pinene, β -pinene and Δ^3 -carene) [Ng *et al.*, 2006]. In the presence of ozone, aerosol mass generated in the photo-oxidation or ozonolysis of terpenes with more than one double bond kept increasing after the hydrocarbon was completely consumed. It is suggested that the secondary products had a significant contribution to the SOA formation of these compounds. Although SOA formed from the photo-oxidation of isoprene also continued growing after the complete consumption of isoprene, the extent of this continued aerosol growth was found much less pronounced than those in the cases of β -caryophyllene and d-limonene. As observed from the

smog chamber experiments, SOA formed from the photo-oxidation of toluene did not show such a continued growth in the presence of ozone after toluene stopped reacting [Hu *et al.*, 2007]. Since higher ozone concentrations were observed on the regional days than the local days, this probably explains the much enhanced SOA formation by monoterpenes and β -caryophyllene estimated on the regional days. SOA formation by monoterpenes, β -caryophyllene, isoprene, and toluene against daily peak O₃ concentration are plotted in Figure 4 for 39 samples (Ozone data were not available at the HKUST site. The 12 samples collected at HKUST are not included in the plot). A two-sided *t* test with (*n*-2) degrees of freedom was carried out and the correlation coefficients were found to be significant [Miller and Miller, 2005], with the correlation with the daily peak ozone the highest for toluene SOA (*r* = 0.88) and lowest for isoprene SOA (*r* = 0.49). It is useful to represent the successive steps of oxidation leading to the production of the quantified SOA tracers in a reduced expression form [Donahue *et al.*, 2005]:

where *k* is the rate-limiting step rate constant, *O_x* is an oxidant, and *X_i* represents the sum of SOA tracer compounds formed from oxidation of *VOC_i*. The production rate of the SOA tracer can be expressed as

$$P_{X_i} = k[VOC_i][O_x]. \quad (3)$$

The positive correlation of SOA tracers with ozone suggests that their production is sensitive to the oxidant level, as one would expect from Eq (3).

We note that high SO₂ concentrations were observed on the regional days as well. Recent laboratory work showed that organosulfates were formed from the oxidation of aromatic compounds, isoprene and monoterpenes in the presence of acidified sulfate seed or SO₂. There is also evidence of their presence in ambient aerosols [Liggio *et al.*, 2004; Surratt *et al.*, 2007a; Surratt *et al.*, 2007b; Iinuma *et al.*, 2007; Gomez-Gonzalez *et al.*, 2008; Jaoui *et al.*,

2008]. The possible contribution of organosulfates to SOA was not counted by this tracer based method because the mass fractions of the SOA tracers were derived from smog chamber experiments, in which neutral sulfate seed aerosols were used [Kleindienst *et al.*, 2007]. It was likely that more organosulfates were present in ambient aerosols collected on the regional days.

In addition to the SOA tracer compounds, noticeable amounts of levoglucosan, hexadecanoic acid and octadecanoic acid were observed in the ambient aerosols, signaling the contributions of biomass burning and cooking emissions. Other known sources for primary OC in Hong Kong are diesel and gasoline exhaust, dust, and vegetative detritus [Zheng *et al.*, 2006]. Although similar time trends of OC mass concentrations and SOC contributions to OC were observed at all four sites, slightly higher average SOC percentage contributions to OC were found at the HKUST and TC sites while higher OC mass concentrations were found at the YL and TW sites (Table 2 and Figure 3). This could be explained by the larger population and greater commercial activities at YL and TW sites than at the other two sites, which resulted in larger fractions of POC contributed by automobile exhaust and cooking to OC.

4. Conclusion

Secondary organic tracer compounds for SOA formed from isoprene, monoterpenes, β -caryophyllene and toluene were identified and quantified in 51 samples collected at four sites in Hong Kong during the summer of 2006. These ambient concentrations of tracer species were used to assess the contributions to SOC and SOA by their respective VOC precursors by using the laboratory-derived organic tracer mass fractions. Monoterpenes and β -caryophyllene were found to be significant contributors to SOA formation in Hong Kong during the summer of 2006. This is consistent with the high annual monoterpene emissions

observed in Hong Kong and also indicates significant sesquiterpene emissions in the area. Higher SOC and SOA contributions and OC mass concentrations were observed on the days mainly influenced by regional sources due to elevated oxidant levels than the days mainly affected by local emissions.

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Table 1. Meteorological parameters, concentrations of select major air pollutants, concentrations of EC, OC, PM_{2.5} and the estimated SOC and SOA contributions by isoprene, monoterpenes, β -caryophyllene and toluene in fine aerosol samples collected at Yuen Long, and the origin of pollution source on each sampling day.

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	YL 060708	YL 060710	YL 060712	YL 060714	YL 060716	YL 060718	YL 060720	YL 060722	YL 060724	YL 060726	YL 060728	YL 060730	YL 060801	YL 060803
Temperature (°C)	30.4	30.1	31.3	32.0	27.9	30.4	30.9	30.7	32.4	29.4	26.9	28.2	30.5	27.2
RH _{average}	74.6%	78.7%	67.6%	69.8%	80.7%	70.5%	65.8%	66.5%	61.2%	77.1%	79.9%	66.9%	59.3%	74.1%
Rainfall (mm)	27.18	3.30 [†]	0 [†]	0.25	64.74 [†]	1.77 [†]	0	0	0	20.58	22.61 [†]	0.25 [†]	0	51.23 [†]
PM _{2.5} ($\mu\text{g m}^{-3}$)	NA ^c	NA ^c	24.2	32.0	10.7	14.3	14.5	15.5	90.7	43.5	10.6	19.6	39.7	9.90
EC ($\mu\text{gC m}^{-3}$)	2.65	1.92	1.80	0.82	0.79	1.67	1.61	1.25	1.82	0.92	1.39	0.82	1.44	1.15
OC ($\mu\text{gC m}^{-3}$)	3.48	4.54	6.46	7.73	2.61	3.64	4.03	5.29	21.6	10.8	4.55	5.33	10.9	2.57
OM ^a ($\mu\text{g m}^{-3}$)	6.60	8.63	12.3	17.0	4.95	6.91	7.65	10.0	47.6	23.7	10.0	10.1	23.9	4.89
SOA _{isoprene} ^b	0.52	0.29	0.27	1.10	0.25	0.04	0.06	0.09	1.64	1.38	0.07	0.13	0.21	0.52
SOA _{monoterpenes}	0.37	0.23	0.47	2.92	0.18	0.07	0.06	0.14	6.02	2.65	0.07	0.66	2.44	0.27
SOA β -caryophyllene	0.11	0.43	0.29	2.05	0.24	0.20	0.18	0.44	5.30	2.44	0.22	0.63	3.17	0.34
SOA _{toluene}	0.26	0.15	0.22	0.69	0.15	0.10	0.08	0.12	1.02	0.72	0.09	0.37	1.61	0.24
Total SOA ^d	1.25	1.09	1.25	6.76	0.83	0.41	0.38	0.79	14.0	7.19	0.45	1.79	7.43	1.37
	(19.0%)	(12.6%)	(10.2%)	(39.7%)	(16.7%)	(5.87%)	(4.99%)	(7.82%)	(29.4%)	(30.3%)	(4.48%)	(17.7%)	(31.1%)	(28.0%)
SOC _{isoprene} ^b ($\mu\text{gC m}^{-3}$)	0.21	0.12	0.11	0.45	0.10	0.02	0.02	0.03	0.67	0.56	0.03	0.05	0.09	0.21
SOC _{monoterpenes}	0.27	0.17	0.34	2.12	0.13	0.05	0.04	0.10	4.38	1.93	0.05	0.48	1.78	0.20
SOC β -caryophyllene	0.05	0.20	0.14	0.97	0.11	0.09	0.09	0.21	2.51	1.15	0.11	0.30	1.50	0.16
SOC _{toluene}	0.13	0.07	0.11	0.35	0.08	0.05	0.04	0.06	0.52	0.36	0.05	0.19	0.82	0.12
Total SOC ^d	0.66	0.56	0.70	3.89	0.42	0.21	0.20	0.41	8.07	4.01	0.23	1.02	4.18	0.69
	(19.0%)	(12.4%)	(10.9%)	(50.3%)	(16.3%)	(5.82%)	(4.85%)	(7.66%)	(37.3%)	(37.2%)	(5.00%)	(19.1%)	(38.5%)	(26.9%)
O ₃ _{average} (ppb)	8.52	7.07	8.94	28.9	13.7	9.71	5.45	7.92	34.9	17.8	6.66	14.0	35.1	20.9
O ₃ _{hourly peak} (ppb)	20.7	11.7	35.7	65.0	25.3	16.6	18.2	21.1	145	31.0	14.3	21.9	127	25.6
SO ₂ _{average} (ppb)	5.22	4.60	9.26	16.1	3.02	8.67	15.6	10.6	33.6	10.6	6.75	4.73	22.2	2.94
SO ₂ _{hourly peak} (ppb)	12.0	6.00	22.7	39.8	3.50	15.4	40.0	17.8	79.7	15.7	21.8	5.70	101	3.40
Origin of pollution source	local	local	local	regional	local	local	local	local	regional	regional	local	local	regional	local

[†] There was rainfall on the previous day. The rainfall amount on the previous day was 6.85 mm on Jul. 09, 8.13 mm on Jul. 11, 7.86 mm on Jul. 15, 6.10 mm on Jul. 17, 50.28 mm on Jul. 27, 40.91 mm on Jul. 29, and 51.53 mm on Aug. 2.

^a A factor of 1.9 was used to estimate the OM from local sources and 2.2 for that from regional sources.

^b SOA and SOC are the total mass concentrations of SOA and SOC produced by isoprene, monoterpene, β -caryophyllene and toluene.

^c Teflon filters were torn on these two sampling days. Therefore no PM_{2.5} mass concentration data were available.

^d The percentage contributions to OC and OM are given in the parentheses.

Table 2. Summary of average concentrations of PM_{2.5} mass, EC, OC, and SOA by individual precursors at four sampling sites under influences of different pollution sources.

	Days influenced by regional sources					Days influenced by local sources				
	YL	TW	TC	HKUST	Four sites (min-max)	YL	TW	TC	HKUST	Four sites (min-max)
Average Concentration										
EC ($\mu\text{gC m}^{-3}$)	2.26	3.18	1.74	1.09	2.06 (0.31 - 3.55)	2.54	3.87	1.40	0.89	2.22 (0.20-5.00)
OC	12.8	12.3	9.01	7.57	10.4 (2.22 - 22.3)	2.88	3.82	2.07	1.79	2.66 (0.61-4.96)
OC/EC	5.55	3.93	5.46	6.86	5.45 (2.60 - 8.48)	1.22	1.08	1.68	2.56	1.60 (0.68-5.43)
SOC _{isoprene}	0.44	0.47	0.47	0.47	0.46 (0.03 - 0.81)	0.09	0.08	0.12	0.06	0.09 (0.01 - 0.29)
SOC _{monoterpenes}	2.55	2.78	2.46	2.18	2.49 (0.54 - 4.82)	0.18	0.19	0.20	0.14	0.18 (0.03 - 0.57)
SOC _{β-caryophyllene}	1.53	2.01	1.58	1.21	1.58 (0.19 - 3.49)	0.15	0.28	0.17	0.08	0.17 (0.05 - 0.61)
SOC _{toluene}	0.51	0.47	0.51	0.39	0.47 (0.25 - 0.82)	0.09	0.09	0.10	0.09	0.09 (0.04 - 0.22)
Total SOC	5.04	5.73	5.01	4.24	5.01 (1.01 - 9.56)	0.51	0.64	0.59	0.37	0.53 (0.16 - 1.60)
PM _{2.5} ($\mu\text{g m}^{-3}$)	51.5	45.0	45.2	40.9	45.6 (15.8 - 90.7)	14.9	15.0	11.9	10.5	13.0 (1.06-24.2)
SOA _{isoprene}	1.08	1.16	1.16	1.15	1.14 (0.07 - 1.99)	0.22	0.20	0.28	0.14	0.21 (0.02-0.70)
SOA _{monoterpenes}	3.51	3.82	3.38	2.99	3.42 (0.75 - 6.63)	0.25	0.26	0.28	0.20	0.24 (0.05-0.78)
SOA _{β-caryophyllene}	3.24	4.24	3.33	2.56	3.34 (0.40 - 7.37)	0.31	0.59	0.35	0.17	0.36 (0.11-1.28)
SOA _{toluene}	1.01	0.93	1.00	0.77	0.93 (0.49 - 1.61)	0.18	0.18	0.20	0.17	0.18 (0.08-0.43)
Total SOA	8.84	10.15	8.87	7.46	8.83 (1.71 - 16.8)	0.96	1.24	1.11	0.68	0.99 (0.30-3.05)
%OC counted by identified SOA	41%	42%	48%	48%	45% (26%-62%)	13%	12%	19%	14%	14% (4%-33%)

Table 3. Measured ambient mass concentrations (ng m^{-3}) of SOA tracer compounds, saccharides and carboxylic acids in fine aerosol samples collected at Yuen Long, Hong Kong during the summer of 2006.

Compound Name	Peak ID**	Concentration (ng m ⁻³)													
		YL 060708	YL 060710	YL 060712	YL 060714	YL 060716	YL 060718	YL 060720	YL 060722	YL 060724	YL 060726	YL 060728	YL 060730	YL 060801	YL 060803
<i>Tracers for isoprene SOA</i>															
2-Methylglyceric acid ^a	4	0.63	0.41	0.45	1.74	0.44	0.11	0.12	0.16	4.58	2.61	0.11	0.58	0.96	0.67
2-Methylthreitol ^a	14	6.26	2.61	3.17	11.2	2.13	0.73	1.02	1.45	43.4	31.6	1.25	2.51	2.38	6.73
2-Methylerythritol ^a	15	26.1	15.1	13.7	56.5	13.5	1.55	2.39	3.78	55.2	52.9	2.88	4.91	10.2	25.2
Cis-2-methyl-1,3,4-trihydroxy-1-butene ^b	5	16.7	5.29	5.81	37.5	4.54	0.14	0.17	0.37	135	37.5	2.66	2.10	6.81	5.73
3-methyl-2,3,4-trihydroxy-1-butene ^b	6	8.27	2.22	2.73	20.2	2.69	0.05	0.06	0.19	53.4	19.4	1.42	0.98	3.43	3.42
Trans-2-methyl-1,3,4-trihydroxy-1-butene ^b	7	31.3	0.40	15.1	49.0	14.0	0.11	0.06	0.21	237	91.3	3.07	6.00	22.8	17.7
Σisoprene tracers (exclude triols)		33.0	18.1	17.3	69.4	16.1	2.38	3.53	5.40	103	87.2	4.25	8.01	13.5	32.6
<i>Tracers for monoterpene SOA</i>															
3-hydroxyglutaric acid ^c	16	33.4	18.0	54.6	200	14.7	3.95	2.43	10.7	370	182	3.39	62.3	199	18.3
3-hydroxy-4,4-dimethylglutaric acid ^c	19	3.84	1.48	2.10	25.4	1.16	0.32	0.27	0.88	51.0	27.8	0.27	5.32	14.3	1.31
3-methyl-1,2,3-butanetricarboxylic acid ^c	28	8.25	8.99	8.12	182	4.99	1.69	1.76	3.38	457	156	1.87	25.6	154	14.9
3-Isopropylpentanedioic acid ^d	26	4.22	3.50	1.86	10.8	2.80	2.18	1.81	2.47	40.6	18.2	1.95	6.90	16.1	4.53
3-Acetyl pentanedioic acid ^d	18	8.59	4.26	10.3	64.5	3.94	1.93	1.86	2.60	80.3	49.5	1.70	7.78	17.8	4.25
3-Acetyl hexanedioic acid ^d	25	3.24	2.79	1.92	6.96	2.44	2.46	2.16	2.87	11.7	11.5	1.97	3.09	9.26	2.67
Σα-pinene tracers		61.6	39.1	78.9	490	30.0	12.5	10.3	22.9	1011	446	11.2	111	410	45.9
<i>Tracers for β-caryophyllene SOA</i>															
β-Caryophyllinic acid ^d	37	1.15	4.64	3.11	22.3	2.59	2.15	2.00	4.78	57.8	26.6	2.42	6.87	34.5	3.69
<i>Tracers for toluene SOA</i>															
2,3-Dihydroxy-4-oxopentanoic acid ^c	11	1.04	0.58	0.89	2.77	0.62	0.39	0.33	0.50	4.11	2.87	0.37	1.48	6.45	0.96
<i>Saccharides</i>															
Levoglucosan ^c	22	25.9	9.98	17.00	62.6	7.94	3.49	5.66	16.4	97.7	55.0	16.6	25.6	35.6	10.6
Glycerol ^c	1	1.60	- [#]	0.59	1.81	1.14	-	-	0.08	7.08	3.90	0.62	0.95	2.70	2.52
Meso-erythritol ^c	13	0.82	0.33	0.66	3.47	0.28	0.11	0.11	0.29	8.12	2.87	0.29	1.34	3.84	0.48
Xylitol ^c	23	0.22	0.16	0.04	2.04	0.01	0.01	-	0.06	3.21	1.89	-	1.01	1.31	0.02
Xylose ^{c,*}	24,29	0.61	0.46	0.82	15.3	0.25	0.23	0.23	0.69	18.4	20.2	0.49	1.08	1.74	0.48

Mannitol ^c	35	-	1.06	0.02	0.86	0.18	0.62	0.35	0.62	1.77	0.77	0.41	0.33	0.26	1.31
Fructose ^{c,*}	30,32	0.77	1.17	0.50	4.82	0.28	0.42	0.43	2.44	16.4	5.88	5.03	4.96	3.86	2.61
Galactosan ^c	20	0.34	0.28	0.86	1.44	0.09	0.11	0.24	0.56	7.37	2.31	0.54	1.14	1.36	0.27
Sucrose ^c	41	0.23	0.64	0.49	0.50	0.17	0.59	0.29	0.69	0.84	0.43	1.71	0.81	0.38	0.69
Mycose ^c	42	0.46	1.14	1.07	1.21	0.46	0.91	0.62	0.94	1.33	1.10	0.17	0.13	0.52	0.43
Arabitol ^c	27	0.72	0.69	0.56	4.09	0.23	0.32	0.29	0.64	1.01	0.90	0.46	0.70	0.47	1.02
Sorbitol ^c	36	0.08	0.19	0.09	0.08	0.15	0.14	0.13	0.19	0.79	0.25	0.19	0.17	0.26	0.23
Glucose ^{c,*}	33,38	0.14	1.15	0.19	4.43	0.42	0.58	0.61	1.28	9.46	10.9	1.21	1.26	0.75	1.44
Mannose ^{c,*}	31,34	0.16	0.32	0.12	1.42	0.15	0.16	0.14	0.23	0.84	0.85	0.24	0.32	0.27	0.33
<i>Dicarboxylic acids</i>															
Succinic acid ^c	3	19.7	7.26	7.00	27.6	17.0	1.26	2.67	7.95	38.6	22.7	5.94	29.4	65.2	37.2
Maleic acid ^c	2	4.44	2.25	2.87	4.57	3.15	2.20	2.13	2.43	39.8	5.35	2.23	5.32	6.60	3.79
Adipic acid ^c	12	7.87	5.87	6.39	10.2	6.22	4.92	4.91	6.76	34.4	13.9	6.03	11.5	29.91	9.76
Phthalic acid ^c	21	1.68	1.45	1.43	3.00	1.41	1.31	1.31	1.45	2.38	2.27	1.43	1.92	6.89	1.53
Malic acid ^c	10	124	44.2	133	475	26.4	10.0	7.19	21.2	494	333	13.1	373	615	31.2
Glutaric acid ^c	8	16.5	5.04	7.80	30.7	13.3	3.72	3.61	5.99	211	65.0	7.81	38.3	94.0	22.7
Pimelic acid ^c	17	2.70	2.16	2.13	4.17	1.98	1.57	1.54	2.28	12.7	4.47	2.16	4.46	6.73	2.41
Citramalic acid ^c	9	5.58	2.62	1.56	12.8	2.63	0.82	0.52	1.66	16.3	16.1	0.83	11.4	40.8	4.01
<i>Other acids</i>															
Palmitic acid ^c	39	11.0	8.64	10.8	9.06	6.98	7.64	8.15	9.61	8.29	6.87	14.9	13.2	14.7	14.3
Palmitoleic acid ^c	40	4.85	4.66	4.98	4.72	4.37	4.50	4.65	5.28	4.93	4.30	5.33	4.81	7.50	5.79

^a Quantified using meso-erythritol

^b Quantified using glycerol

^c Quantified using citramalic acid

^d Quantified using pimelic acid

^e Quantified using authentic standards

* Include both α - and β - isomers

The dash (-) denotes that the measured concentration was less than 0.01 ng m⁻³.

** The peak ID refers to the peak labels in Figure 2.

Figure 1. Locations of the four sampling sites in Hong Kong

Figure 2. Total ion chromatogram (TIC) for a trimethylsilylated sample extract. The sample was taken at Tsuen Wan, Hong Kong during the summer of 2006. Peaks were normalized to the highest peak in each section (During the time windows marked with an asterisk (*), the filament was off to avoid the huge impurity peaks)

Figure 3. SOC contributions by different hydrocarbon precursors and the percentage of total SOC apportioned to the identified precursors in ambient OC in individual samples at (a) YL, (b) TW, (c) HKUST and (d) TC. Samples collected on days influenced by regional transport are marked with an asterisk (*).

Figure 4. The relationship between the daily peak ozone concentration and SOC by β -caryophyllene, monoterpenes, toluene, and isoprene.

Contributions of Isoprene, Monoterpenes, β -Caryophyllene, and Toluene to Secondary Organic Aerosols in Hong Kong during the Summer of 2006

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Supplementary materials

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Table S2. Measured ambient mass concentrations (ng m^{-3}) of SOA tracer compounds, saccharides and dicarboxylic acids in fine aerosol samples collected at Tung Chung, Hong Kong during the summer of 2006.

Table S3. Measured ambient mass concentrations (ng m^{-3}) of SOA tracer compounds, saccharides and dicarboxylic acids in fine aerosol samples collected at Hong Kong University of Science and Technology, Hong Kong during the summer of 2006.

Table S4. Concentrations of EC, OC, $\text{PM}_{2.5}$, and the estimated total SOC and SOA contributions as well as the individual contribution of isoprene, monoterpenes, β -caryophyllene and toluene in fine aerosol samples collected at Tsuen Wan, Hong Kong during the summer of 2006. Hourly peak and daily average concentrations of SO_2 and O_3 , temperature, and the origin of pollution source on each sampling day. The percentage contributions to OC and OM are given in the parentheses.

Table S5. Concentrations of EC, OC, $\text{PM}_{2.5}$, and the estimated total SOC and SOA contributions as well as the individual contribution of isoprene, monoterpenes, β -caryophyllene and toluene in fine aerosol samples collected at Tung Chung, Hong Kong during the summer of 2006. Hourly peak and daily average concentrations of SO_2 and O_3 , temperature, relative humidity, and the origin of pollution source on each sampling day. The percentage contributions to OC and OM are given in the parentheses.

Table S6. Concentrations of EC, OC, $\text{PM}_{2.5}$, and the estimated total SOC and SOA contributions as well as the individual contribution of isoprene, monoterpenes, β -caryophyllene and toluene in fine aerosol samples collected at Hong Kong University of Science and Technology, Hong Kong during the summer of 2006. Temperature, relative humidity, and the origin of pollution source on each sampling day. The percentage contributions to OC and OM are given in the parentheses.

Figure S1. Backward trajectories of air masses arriving Hong Kong on the regional days (Hong Kong local time = UTC + 8)

Figure S2 EI mass spectrum of the TMS-derivative of tentatively identified 2,3-dihydroxy-4-oxopentanoic acid in the derivatized extract of $\text{PM}_{2.5}$ aerosols collected in Hong Kong.

Table S1. Measured ambient mass concentrations (ng m⁻³) of SOA tracer compounds, saccharides and dicarboxylic acids in fine aerosol samples collected at Tsuen Wan, Hong Kong during the summer of 2006.

Aerosol samples collected at Tsuen Wan, Hong Kong during the summer of 2000.														
Compound Name	ID	Concentration (ng m ⁻³)												
		TW 060708	TW 060710	TW 060712	TW 060714	TW 060716	TW 060718	TW 060720	TW 060722	TW 060724	TW 060726	TW 060728	TW 060730	TW 060801
<i>Tracers for isoprene SOA</i>														
2-Methylglyceric acid ^b	4	1.02	0.82	0.80	2.20	0.57	0.24	0.15	0.15	4.94	2.20	0.27	0.37	0.59
2-Methylthreitol ^b	14	7.41	3.66	3.68	13.2	1.82	0.87	1.17	1.22	46.5	29.5	1.74	1.22	1.75
2-Methylerythritol ^b	15	26.4	23.3	10.5	67.7	8.90	2.85	3.36	3.70	60.9	55.7	6.57	2.60	7.51
Cis-2-methyl-1,3,4-trihydroxy-1-butene ^c	5	12.7	12.6	6.24	32.0	2.77	0.21	0.25	0.30	61.84	41.2	4.12	1.53	3.19
3-methyl-2,3,4-trihydroxy-1-butene ^c	6	6.74	6.49	3.06	26.3	1.62	0.06	0.11	0.08	43.8	18.2	2.02	0.75	1.66
Trans-2-methyl-1,3,4-trihydroxy-1-butene ^c	7	35.9	19.6	10.8	122	7.83	0.04	0.08	0.02	169	99.5	11.4	4.67	10.1
Σisoprene tracers (exclude triols)		34.8	27.8	15.0	83.2	11.3	3.96	4.68	5.07	112	87.4	8.59	4.19	9.85
<i>Tracers for monoterpene SOA</i>														
3-hydroxyglutaric acid ^d	16	31.6	22.0	38.7	274	10.3	4.84	2.60	4.87	389	192	11.0	73.7	105
3-hydroxy-4,4-dimethylglutaric acid ^d	19	2.98	2.02	2.29	40.3	0.77	0.24	0.35	0.32	55.5	31.5	1.58	5.91	9.27
3-methyl-1,2,3-butanetricarboxylic acid ^d	28	9.05	10.4	9.44	355	3.78	1.71	1.90	1.83	428	195	3.90	30.1	87.1
3-Isopropylpentanedioic acid ^e	26	5.61	3.63	4.26	22.0	2.71	2.09	2.69	2.88	45.8	25.1	2.99	8.58	10.4
3-Acetyl pentanedioic acid ^e	18	9.99	5.36	6.97	96.6	3.33	2.16	1.73	1.74	86.6	51.8	3.07	8.72	10.8
3-Acetyl hexanedioic acid ^e	25	4.75	3.16	2.32	7.31	2.53	2.45	1.51	2.33	22.6	18.4	2.39	3.89	4.81
Σmonoterpene tracers		64.0	46.6	64.0	796	23.4	13.5	10.8	14.0	1027	514	24.9	131	228
<i>Tracers for β-caryophyllene SOA</i>														
β-Caryophyllinic acid ^e	37	1.18	10.2	9.48	48.0	3.90	3.36	2.42	3.15	80.3	34.9	13.8	10.4	21.8
<i>Tracers for toluene SOA</i>														
2,3-Dihydroxy-4-oxopentanoic acid ^d	11	1.00	0.80	0.89	2.76	0.54	0.41	0.35	0.38	5.91	2.84	0.56	1.64	3.36
<i>Saccharides</i>														
Levoglucoan ^a	22	7.67	8.33	12.5	51.2	5.14	2.89	5.58	7.53	66.0	45.7	31.5	32.2	18.0
Glycerol ^a	1	4.59	1.54	1.50	3.97	2.04	-	-	-	7.46	3.82	1.78	0.77	2.22
Meso-erythritol ^a	13	0.87	0.45	0.57	3.25	0.19	0.23	0.16	0.24	8.44	2.74	0.70	1.75	1.90
Xylitol ^a	23	0.09	0.04	0.16	1.18	-	-	0.00	-	4.96	2.19	-	1.06	0.69
Xylose ^{a,*}	24,29	0.72	0.58	0.94	14.8	0.35	0.26	0.26	0.49	17.6	17.9	1.06	1.16	1.10

Mannitol ^a	35	-	1.20	2.13	0.60	0.45	0.56	2.99	2.55	1.53	1.05	1.20	0.80	0.66
Fructose ^{a,*}	30,32	0.66	1.47	1.72	7.58	0.90	1.16	1.12	2.65	16.3	5.39	8.00	6.42	3.00
Galactosan ^a	20	0.22	0.31	0.40	1.63	0.07	0.15	0.37	0.37	3.59	1.98	0.57	0.86	0.63
Sucrose ^a	41	0.55	0.92	0.66	1.27	0.63	1.74	0.88	0.80	1.05	0.74	1.68	0.95	0.46
Mycose ^a	42	0.65	1.16	2.27	2.21	0.76	1.10	3.67	2.33	2.18	1.81	0.26	0.33	0.76
Arabitol ^a	27	1.22	0.96	1.99	5.22	0.43	0.47	4.67	4.98	0.95	0.89	1.22	0.93	0.97
Sorbitol ^a	36	0.09	0.27	0.17	0.09	0.18	0.11	0.39	0.27	0.46	0.17	0.49	0.18	0.14
Glucose ^{a,*}	33,38	0.10	1.65	1.20	5.30	0.86	1.17	2.34	2.20	9.26	10.3	2.31	1.84	0.84
Mannose ^{a,*}	31,34	0.22	0.38	0.54	2.05	0.18	0.20	0.36	0.39	0.84	0.72	0.37	0.48	0.34
<i>Dicarboxylic acid</i>														
Succinic acid ^a	3	30.3	20.4	13.1	27.2	22.6	4.77	4.19	4.33	44.1	28.1	22.2	22.1	49.8
Maleic acid ^a	2	4.47	2.85	3.62	7.06	2.86	2.25	2.13	2.11	15.2	5.79	4.56	5.69	5.31
Adipic Acid ^a	12	9.03	7.62	8.88	15.9	6.81	6.88	5.71	6.13	32.8	13.6	9.15	10.9	22.0
Phthalic acid ^a	21	1.70	1.52	1.66	4.27	1.38	1.35	1.35	1.36	2.70	2.35	1.71	2.09	3.51
DL-Malic acid ^a	10	61.4	43.3	66.2	662	18.7	11.3	9.25	9.53	566	357	31.9	432	299
Glutaric acid ^a	8	22.1	15.1	18.8	55.9	15.6	4.68	3.85	4.18	213	55.4	16.6	22.7	47.8
Pimelic acid ^a	17	3.56	2.90	3.45	7.05	2.32	2.32	1.91	2.09	12.4	5.17	3.59	4.41	6.04
Citramalic acid ^a	9	5.76	3.58	2.02	17.5	2.42	1.21	0.61	0.75	24.2	17.5	1.88	11.9	25.7
Palmitic acid ^a	39	17.6	11.5	11.7	12.0	9.57	10.0	9.91	9.95	9.07	9.75	15.0	14.9	16.1
Palmitoleic acid ^a	40	2.69	7.26	5.38	7.84	4.82	5.99	6.74	6.93	5.96	5.26	7.06	7.56	8.68

^a Quantified using authentic standards

^b Quantified using meso-erythritol

^c Quantified using glycerol

^d Quantified using citramalic acid

^e Quantified using pimelic acid

* Include both α - and β - isomers

The dash (-) denotes that the measured concentration was less than 0.01 ng m⁻³.

Table S2. Measured ambient mass concentrations (ng m⁻³) of SOA tracer compounds, saccharides and dicarboxylic acids in fine aerosol samples collected at Tung Chung, Hong Kong during the summer of 2006

Compound Name	ID	Concentration (ng m ⁻³)											
		TC 060710	TC 060712	TC 060714	TC 060716	TC 060718	TC 060720	TC 060724	TC 060726	TC 060728	TC 060730	TC 060801	TC 060803
<i>Tracers for isoprene SOA</i>													
2-Methylglyceric acid ^b	4	0.38	0.92	1.41	0.18	0.77	0.15	5.90	2.35	0.16	0.49	0.70	0.45
2-Methylthreitol ^b	14	3.57	9.19	20.8	3.08	1.86	2.76	55.2	32.0	1.63	1.08	2.75	3.43
2-Methylerythritol ^b	15	27.9	34.2	53.0	18.2	3.92	7.91	64.1	50.5	4.30	1.36	4.02	15.9
Cis-2-methyl-1,3,4-trihydroxy-1-butene ^c	5	9.53	16.6	45.2	3.46	0.74	0.66	77.0	35.2	2.30	0.83	4.20	4.15
3-methyl-2,3,4-trihydroxy-1-butene ^c	6	10.4	8.27	22.1	2.16	0.42	0.33	53.3	16.5	1.00	0.37	2.03	2.41
Trans-2-methyl-1,3,4-trihydroxy-1-butene ^c	7	23.9	24.1	47.1	11.1	0.17	0.11	176	69.5	1.11	1.54	8.80	13.0
Σisoprene tracers (exclude triols)		31.8	44.3	75.2	21.5	6.56	10.8	125	84.9	6.10	2.92	7.47	19.8
<i>Tracers for monoterpene SOA</i>													
3-hydroxyglutaric acid ^d	16	31.1	79.9	161	10.0	9.29	3.05	417	149	2.51	47.7	126	12.7
3-hydroxy-4,4-dimethylglutaric acid ^d	19	3.48	5.14	31.0	0.58	0.78	0.34	64.1	30.3	0.19	3.82	8.51	0.85
3-methyl-1,2,3-butanetricarboxylic acid ^d	28	4.06	21.1	170	3.37	2.25	1.98	477	190	0.82	21.5	90.8	9.67
3-Isopropylpentanedioic acid ^e	26	4.31	5.47	15.4	1.96	2.13	1.79	46.9	18.7	1.38	5.45	11.1	1.82
3-Acetyl pentanedioic acid ^e	18	7.43	10.0	63.0	2.96	2.61	1.63	85.8	51.3	1.40	7.01	12.1	2.88
3-Acetyl hexanedioic acid ^e	25	2.98	2.76	8.98	2.02	2.56	2.07	23.7	13.7	1.77	2.96	5.63	2.24
Σmonoterpene tracers		53.4	124	449	21.0	19.6	10.9	1115	454	8.07	88.5	254	30.2
<i>Tracers for β-caryophyllene SOA</i>													
β-Caryophyllinic acid ^e	37	1.35	14.0	25.0	1.71	1.77	1.77	71.6	23.0	1.24	5.19	25.7	2.13
<i>Tracers for toluene SOA</i>													
2,3-Dihydroxy-4-oxopentanoic acid ^d	11	0.94	1.33	2.50	0.61	0.52	0.38	6.43	3.01	0.35	1.51	4.03	0.72
<i>Saccharides</i>													
Levoglucosan ^a	22	4.78	22.7	50.8	3.45	2.17	3.76	48.1	46.0	2.66	8.10	16.4	3.07
Glycerol ^a	1	1.13	2.05	2.08	1.25	0.12	0.04	5.96	2.56	0.20	0.40	1.46	2.20
Meso-erythritol ^a	13	0.66	1.40	2.30	0.32	0.15	0.16	8.92	2.61	0.09	1.21	2.66	0.23
Xylitol ^a	23	0.17	0.70	1.81	0.02	0.06	0.04	6.41	2.38	-	0.84	1.11	-
Xylose ^{a,*}	24,29	0.42	2.15	15.7	0.22	0.20	0.26	24.4	22.6	0.18	0.54	1.27	0.26
Mannitol ^a	35	0.09	7.03	4.29	0.48	0.48	1.13	1.85	0.95	0.19	0.28	0.45	0.21

Fructose ^{a,*}	30,32	0.24	4.42	6.90	0.36	0.31	1.00	12.1	4.72	0.38	0.86	2.66	0.21
Galactosan ^a	20	0.16	0.95	0.88	0.06	0.20	0.37	2.08	3.20	0.10	0.37	0.90	0.03
Sucrose ^a	41	0.02	2.01	1.64	1.44	0.33	0.89	0.48	0.14	0.21	-	0.72	0.33
Mycose ^a	42	0.49	3.81	3.26	0.78	0.77	1.36	1.94	1.34	0.11	0.11	0.29	0.13
Arabitol ^a	27	0.66	5.11	3.09	0.43	0.33	0.67	2.16	1.39	0.19	0.50	0.81	0.25
Sorbitol ^a	36	0.11	0.70	0.42	0.16	0.14	0.20	0.30	0.17	0.12	0.16	0.18	0.12
Glucose ^{a,*}	33,38	0.17	6.32	7.89	0.65	0.54	1.31	9.44	9.58	0.36	0.80	0.62	0.36
Mannose ^{a,*}	31,34	0.18	1.52	1.50	0.22	0.24	0.34	1.14	0.79	0.17	0.24	0.19	0.14
<i>Dicarboxylic acid</i>													
Succinic acid ^a	3	10.7	20.5	24.6	13.5	6.58	3.47	47.4	24.3	4.98	26.6	41.7	24.2
Maleic acid ^a	2	3.47	3.78	4.83	2.87	2.24	2.19	34.4	6.51	2.18	5.44	5.65	3.25
Adipic Acid ^a	12	7.46	9.54	11.1	6.01	5.48	5.33	31.3	12.6	5.27	10.4	41.4	8.00
Phthalic acid ^a	21	1.60	1.88	2.68	1.40	1.35	1.31	2.47	2.69	1.34	2.88	5.23	1.47
DL-Malic acid ^a	10	109	191	415	34.3	27.2	13.4	598	291	9.99	300	395	23.6
Glutaric acid ^a	8	15.1	20.7	21.9	12.6	4.82	4.06	171	50.6	5.21	29.9	131	16.9
Pimelic acid ^a	17	3.06	2.98	4.15	1.94	1.83	1.82	13.1	4.38	1.75	3.03	5.76	2.03
Citramalic acid ^a	9	4.39	6.11	11.7	3.19	2.09	0.83	23.5	14.5	0.69	9.24	30.4	3.32
Palmitic acid ^a	39	10.9	13.3	7.59	7.04	8.05	8.92	9.44	9.22	11.2	9.42	13.5	11.1
Palmitoleic acid ^a	40	4.71	4.46	4.38	4.23	4.06	2.61	6.68	4.86	5.97	4.77	5.29	5.55

^a Quantified using authentic standards

^b Quantified using meso-erythritol

^c Quantified using glycerol

^d Quantified using citramalic acid

^e Quantified using pimelic acid

* Include both α - and β - isomers

The dash (-) denotes that the measured concentration was less than 0.01 ng m⁻³.

Table S3. Measured ambient mass concentrations (ng m^{-3}) of SOA tracer compounds, saccharides and dicarboxylic acids in fine aerosol samples collected at Hong Kong University of Science and Technology, Hong Kong during the summer of 2006.

Aerosol samples collected at Hong Kong University of Science and Technology, Hong Kong during the summer of 2000.													
Compound Name	ID	Concentration (ng m ⁻³)											
		UST 060712	UST 060714	UST 060716	UST 060718	UST 060720	UST 060722	UST 060724	UST 060726	UST 060728	UST 060730	UST 060801	UST 060803
<i>Tracers for isoprene SOA</i>													
2-Methylglyceric acid ^b	4	0.83	1.36	0.55	0.19	0.33	0.08	4.67	3.00	0.12	0.43	0.21	0.20
2-Methylthreitol ^b	14	9.78	19.7	1.95	0.47	1.37	0.46	44.2	32.0	0.36	0.30	1.31	0.95
2-Methylerythritol ^b	15	30.4	55.1	10.9	1.13	2.72	0.74	54.2	69.7	0.96	0.44	2.95	3.60
Cis-2-methyl-1,3,4-trihydroxy-1-butene ^c	5	10.4	36.5	2.23	0.23	0.47	0.02	75.3	51.1	1.59	0.51	1.18	2.22
3-methyl-2,3,4-trihydroxy-1-butene ^c	6	5.02	20.6	1.38	0.08	0.18	-	44.2	18.7	0.74	0.22	1.15	1.31
Trans-2-methyl-1,3,4-trihydroxy-1-butene ^c	7	26.6	67.6	7.17	-	0.09	-	202	106	3.83	1.80	1.85	7.14
Σisoprene tracers (exclude triols)		41.0	76.1	13.4	1.79	4.41	1.28	103	105	1.44	1.17	4.47	4.76
<i>Tracers for monoterpene SOA</i>													
3-hydroxyglutaric acid ^d	16	46.0	179	8.23	5.30	2.73	3.95	307	216	3.21	65.8	80.5	7.20
3-hydroxy-4,4-dimethylglutaric acid ^d	19	2.92	26.3	0.96	0.35	0.21	0.14	42.0	28.8	0.30	4.61	8.35	0.74
3-methyl-1,2,3-butanetricarboxylic acid ^d	28	4.34	224	3.49	0.93	1.24	1.79	321	248	1.58	25.6	24.0	5.26
3-Isopropylpentanedioic acid ^e	26	3.91	13.6	2.59	1.60	2.40	1.55	32.9	24.2	1.37	7.23	4.47	1.57
3-Acetyl pentanedioic acid ^e	18	8.02	52.7	3.53	2.56	1.62	1.58	65.8	59.0	1.68	8.25	6.22	2.25
3-Acetyl hexanedioic acid ^e	25	3.78	7.44	2.40	2.18	2.22	1.85	18.6	18.6	1.79	3.43	1.87	1.73
Σα-pinene tracers		69.0	503	21.2	12.9	10.4	10.9	787	595	9.93	115	125	18.8
<i>Tracers for β-caryophyllene SOA</i>													
β-Caryophyllinic acid ^e	37	1.33	24.8	1.73	1.25	1.48	1.32	57.0	25.3	1.30	4.87	4.37	1.75
<i>Tracers for toluene SOA</i>													
2,3-Dihydroxy-4-oxopentanoic acid ^d	11	0.95	2.40	0.53	0.42	0.38	0.40	4.82	3.06	0.38	1.71	1.98	0.55
<i>Saccharides</i>													
Levogluocan ^a	22	14.7	46.6	3.21	2.11	4.13	1.84	39.8	50.7	1.67	6.16	7.98	2.34
Glycerol ^a	1	3.52	4.02	1.56	-	0.06	-	5.20	3.99	0.41	0.32	0.23	2.02
Meso-erythritol ^a	13	0.82	2.98	0.21	0.11	0.20	0.06	8.11	4.08	0.07	1.76	0.89	0.17
Xylitol ^a	23	0.07	1.61	0.01	-	-	0.04	3.55	2.23	-	1.00	0.54	-
Xylose ^{a,*}	24,29	0.84	14.7	0.22	0.15	0.28	0.15	14.7	21.7	0.12	0.52	0.65	0.19

Mannitol ^a	35	-	0.72	0.29	0.34	2.82	0.25	2.20	1.54	-	0.07	0.50	0.05
Fructose ^{a,*}	30,32	0.54	6.80	0.31	0.21	2.27	0.26	10.7	6.80	0.06	0.70	2.68	0.21
Galactosan ^a	20	0.62	1.87	0.05	0.06	0.17	0.06	2.43	3.25	-	0.33	0.35	-
Sucrose ^a	41	-	1.47	0.10	0.37	2.52	0.30	1.54	0.59	0.14	-	0.65	0.25
Mycose ^a	42	0.37	2.66	0.61	0.92	3.10	0.55	2.06	2.13	0.05	0.09	0.21	0.06
Arabitol ^a	27	0.42	3.25	0.28	0.31	1.77	0.23	1.08	2.92	0.06	0.64	0.38	0.13
Sorbitol ^a	36	0.08	0.15	0.11	0.11	0.26	0.14	0.40	0.22	0.10	0.13	0.15	0.11
Glucose ^{a,*}	33,38	0.11	6.24	0.47	0.22	2.32	0.44	6.48	11.6	0.18	0.54	0.59	0.27
Mannose ^{a,*}	31,34	0.11	1.41	0.17	0.13	0.49	0.13	0.76	1.01	0.10	0.20	0.17	0.11
<i>Dicarboxylic acid</i>													
Succinic acid ^a	3	25.6	17.4	17.2	4.70	5.50	3.30	38.9	42.5	8.19	32.7	8.84	26.1
Maleic acid ^a	2	4.16	5.34	3.07	2.29	2.29	2.17	15.8	7.24	2.66	4.91	2.67	2.91
Adipic Acid ^a	12	9.41	11.9	5.94	5.27	5.75	5.08	28.3	14.2	5.84	10.4	8.58	7.16
Phthalic acid ^a	21	1.79	3.14	1.40	1.32	1.35	1.35	2.41	2.86	1.38	2.04	1.52	1.43
DL-Malic acid ^a	10	76.1	404	22.2	16.1	11.6	12.1	509	376	10.3	407	268	15.7
Glutaric acid ^a	8	22.8	36.3	13.0	4.13	4.24	3.61	159	60.6	7.97	38.6	14.0	12.1
Pimelic acid ^a	17	2.93	4.62	1.95	1.71	1.75	1.67	10.2	4.83	1.92	3.03	3.38	1.78
Citramalic acid ^a	9	4.74	9.67	2.29	1.64	0.85	1.04	19.0	21.6	0.89	12.4	15.0	1.90
Palmitic acid ^a	39	12.0	9.54	7.17	7.05	9.88	7.60	8.28	12.4	8.88	8.35	13.5	9.88
Palmitoleic acid ^a	40	5.15	6.09	5.20	4.18	7.92	3.81	5.67	7.10	5.41	4.70	5.15	5.57

^a Quantified using authentic standards

^b Quantified using meso-erythritol

^c Quantified using glycerol

^d Quantified using citramalic acid

^e Quantified using pimelic acid

* Include both α - and β - isomers

The dash (-) denotes that the measured concentration was less than 0.01 ng m⁻³.

Table S4. Concentrations of EC, OC, PM_{2.5}, and the estimated total SOC and SOA contributions as well as the individual contribution of isoprene, monoterpenes, β -caryophyllene and toluene in fine aerosol samples collected at Tsuen Wan, Hong Kong during the summer of 2006. Hourly peak and daily average concentrations of SO₂ and O₃, temperature, and the origin of pollution source on each sampling day. The percentage contributions to OC and OM are given in the parentheses.

	TW 060708	TW 060710	TW 060712	TW 060714	TW 060716	TW 060718	TW 060720	TW 060722	TW 060724	TW 060726	TW 060728	TW 060730	TW 060801
Temperature (°C)	29.7	29.8	30.6	31.4	27.9	30.5	30.6	30.9	31.3	29.0	27.0	28.7	30.7
Concentration ($\mu\text{g m}^{-3}$)													
PM _{2.5}	13.1	12.7	20.5	29.0	12.7	9.90	14.0	15.5	84.6	38.7	13.7	22.5	27.4
EC	3.64	4.16	3.20	1.37	3.05	3.29	1.74	1.59	0.82	1.72	4.10	0.96	1.15
OC	4.07	5.67	7.21	11.8	3.15	5.24	5.01	6.30	23.2	10.3	6.39	6.06	9.35
OM ^a	7.74	10.8	13.7	25.9	5.98	9.95	9.52	12.0	51.1	22.6	14.1	11.5	20.6
SOA _{isoprene} ^b	0.55	0.44	0.24	1.32	0.18	0.06	0.07	0.08	1.78	1.39	0.14	0.07	0.16
SOA _{monoterpenes}	0.38	0.28	0.38	4.74	0.14	0.08	0.06	0.08	6.11	3.06	0.15	0.78	1.36
SOA _{β-caryophyllene}	0.11	0.93	0.87	4.40	0.36	0.31	0.22	0.29	7.37	3.20	1.27	0.96	2.00
SOA _{toluene}	0.25	0.20	0.22	0.69	0.14	0.10	0.09	0.10	1.48	0.71	0.14	0.41	0.84
Total SOA	1.29	1.85	1.71	11.1	0.81	0.55	0.45	0.55	16.7	8.36	1.69	2.21	4.36
	(16.7%)	(17.2%)	(12.5%)	(43.0%)	(13.6%)	(5.56%)	(4.70%)	(4.58%)	(32.8%)	(37.0%)	(12.0%)	(19.2%)	(21.2%)
SOC _{isoprene} ^b ($\mu\text{gC m}^{-3}$)	0.22	0.18	0.10	0.54	0.07	0.03	0.03	0.03	0.72	0.56	0.06	0.03	0.06
SOC _{monoterpenes}	0.28	0.20	0.28	3.44	0.10	0.06	0.05	0.06	4.45	2.23	0.11	0.57	0.99
SOC _{β-caryophyllene}	0.05	0.44	0.41	2.09	0.17	0.15	0.11	0.14	3.49	1.52	0.60	0.45	0.95
SOC _{toluene}	0.13	0.10	0.11	0.35	0.07	0.05	0.04	0.05	0.75	0.36	0.07	0.21	0.43
Total SOC	0.68	0.92	0.90	6.42	0.41	0.28	0.23	0.28	9.41	4.67	0.84	1.25	2.42
	(16.7%)	(16.3%)	(12.5%)	(54.4%)	(13.1%)	(5.38%)	(4.52%)	(4.42%)	(40.5%)	(45.5%)	(13.1%)	(20.7%)	(26.0%)
Concentration (ppb)													
O ₃ _{average}	3.73	2.81	4.04	14.4	4.04	4.22	5.78	4.29	27.6	9.79	4.70	12.7	23.0
O ₃ _{hourly peak}	8.40	7.90	11.1	42.7	21.9	10.8	13.5	11.5	103	21.4	7.30	26.9	85.9
SO ₂ _{average}	1.90	14.9	6.16	15.8	10.8	17.6	6.25	11.2	23.6	12.0	4.05	3.48	9.52
SO ₂ _{hourly peak}	2.00	23.2	11.1	53.1	25.7	51.7	10.1	30.0	50.8	23.5	10.4	5.00	34.0
Origin of pollution source	local	local	local	regional	local	local	local	local	regional	regional	local	local	regional

^a A factor of 1.9 was used to estimate the OM from local sources and 2.2 for that from regional sources.

^b SOA and SOC are the total mass concentrations of SOA and SOC produced by isoprene, monoterpene, β -caryophyllene and toluene.

[#] Relative humidity data was not available for TW site.

Table S5. Concentrations of EC, OC, PM_{2.5}, and the estimated total SOC and SOA contributions as well as the individual contribution of isoprene, monoterpenes, β -caryophyllene and toluene in fine aerosol samples collected at Tung Chung, Hong Kong during the summer of 2006. Hourly peak and daily average concentrations of SO₂ and O₃, temperature, relative humidity, and the origin of pollution source on each sampling day. The percentage contributions to OC and OM are given in the parentheses.

	TC 060710	TC 060712	TC 060714	TC 060716	TC 060718	TC 060720	TC 060724	TC 060726	TC 060728	TC 060730	TC 060801	TC 060803
Temperature (°C)	30.9	31.5	32.9	28.9	30.6	30.1	31.8	30.4	27.1	28.1	30.5	26.7
RH _{average}	77.9%	71.1%	68.4%	81.6%	72.1%	63.8%	62.2%	71.7%	82.9%	73.1%	59.7%	78.6%
Concentration ($\mu\text{g m}^{-3}$)												
PM _{2.5}	1.06 ^d	17.3	24.7	10.9	11.9	10.0	75.2	39.7	NA	20.0	41.1	5.45
EC	1.09	1.79	0.64	0.33	0.88	1.17	0.72	0.89	0.66	1.16	1.00	0.22
OC	2.94	5.10	7.22	1.85	2.67	2.87	15.5	7.64	1.51	5.15	9.88	1.44
OM ^a	5.58	9.70	15.9	3.52	5.07	5.44	34.0	16.8	3.33	9.79	21.7	2.73
SOA _{isoprene} ^b	0.51	0.70	1.19	0.34	0.10	0.17	1.99	1.35	0.10	0.05	0.12	0.31
SOA _{monoterpenes}	0.32	0.74	2.67	0.12	0.12	0.06	6.63	2.70	0.05	0.53	1.51	0.18
SOA β -caryophyllene	0.12	1.28	2.28	0.16	0.16	0.16	6.57	2.10	0.11	0.48	2.36	0.20
SOA _{toluene}	0.23	0.33	0.63	0.15	0.13	0.09	1.61	0.75	0.09	0.38	1.01	0.18
Total SOA	1.18	3.05	6.77	0.78	0.51	0.49	16.8	6.90	0.35	1.43	4.99	0.87
	(21.2%)	(31.5%)	(42.6%)	(22.1%)	(10.1%)	(9.04%)	(49.4%)	(41.1%)	(10.4%)	(14.6%)	(23.0%)	(31.8%)
SOC _{isoprene} ^b ($\mu\text{gC m}^{-3}$)	0.21	0.29	0.48	0.14	0.04	0.07	0.81	0.55	0.04	0.02	0.05	0.13
SOC _{monoterpenes}	0.23	0.54	1.94	0.09	0.08	0.05	4.82	1.96	0.03	0.38	1.10	0.13
SOC β -caryophyllene	0.06	0.61	1.08	0.07	0.08	0.08	3.11	1.00	0.05	0.23	1.12	0.09
SOC _{toluene}	0.12	0.17	0.32	0.08	0.07	0.05	0.81	0.38	0.04	0.19	0.51	0.09
Total SOC	0.61	1.60	3.83	0.38	0.27	0.24	9.56	3.89	0.17	0.82	2.77	0.44
	(20.9%)	(31.3%)	(53.0%)	(20.6%)	(10.1%)	(8.42%)	(61.9%)	(50.9%)	(11.4%)	(15.9%)	(28.1%)	(30.7%)
Concentration (ppb)												
O ₃ _{average}	13.6	9.30	27.8	17.6	15.5	7.84	45.1	32.9	16.0	24.4	46.5	22.2
O ₃ _{hourly peak}	19.1	23.7	55.2	20.2	21.6	16.4	152	49.7	25.0	52.2	154	26.4
SO ₂ _{average}	3.09	3.12	6.80	2.24	2.05	3.21	13.4	7.82	4.89	6.59	26.9	2.36
SO ₂ _{hourly peak}	4.20	5.90	25.1	2.50	2.20	4.40	32.7	11.1	8.60	8.60	117	4.70
Origin of pollution source	local	local	regional	local	local	local	regional	regional	local	local	regional	local

^a A factor of 1.9 was used to estimate the OM from local sources and 2.2 for that from regional sources.

^b SOA and SOC are the total mass concentrations of SOA and SOC produced by isoprene, monoterpene, β -caryophyllene and toluene.

Table S6. Concentrations of EC, OC, PM_{2.5}, and the estimated total SOC and SOA contributions as well as the individual contribution of isoprene, monoterpenes, β -caryophyllene and toluene in fine aerosol samples collected at the Hong Kong University of Science and Technology, Hong Kong during the summer of 2006. Temperature, relative humidity, and the origin of pollution source on each sampling day. The percentage contributions to OC and OM are given in the parentheses.

	UST 060712	UST 060714	UST 060716	UST 060718	UST 060720	UST 060722	UST 060724	UST 060726	UST 060728	UST 060730	UST 060801	UST 060803
Temperature (°C)	30.0	31.4	28.1	28.4	29.7	28.8	29.8	29.5	25.6	26.9	27.9	26.7
RH _{average}	76.2%	67.7%	80.4%	84.1%	72.4%	78.6%	76.2%	71.3%	89.0%	82.7%	79.0%	81.6%
Concentration ($\mu\text{g m}^{-3}$)												
PM _{2.5}	16.2	28.0	2.72	12.1	12.7	7.36	77.4	42.3	NA ^c	18.0	15.8	4.51
EC	0.41	0.79	0.22	0.60	0.99	0.10	1.34	0.97	0.08	0.34	0.24	0.10
OC	4.12	8.37	1.97	2.64	4.06	1.84	14.4	7.99	2.09	2.86	3.02	1.32
OM ^a	7.83	18.4	3.75	5.01	7.72	3.50	31.7	17.6	4.60	5.44	6.64	2.52
SOA _{isoprene} ^b	0.65	1.21	0.21	0.03	0.07	0.02	1.64	1.66	0.02	0.02	0.07	0.08
SOA _{monoterpenes}	0.41	3.00	0.13	0.08	0.06	0.06	4.68	3.54	0.06	0.68	0.75	0.11
SOA _{β-caryophyllene}	0.12	2.27	0.16	0.11	0.14	0.12	5.23	2.32	0.12	0.45	0.40	0.16
SOA _{toluene}	0.24	0.60	0.13	0.10	0.10	0.10	1.21	0.77	0.10	0.43	0.49	0.14
Total SOA	1.42	7.08	0.63	0.32	0.36	0.31	12.8	8.29	0.30	1.58	1.71	0.49
	(18.1%)	(38.5%)	(16.8%)	(6.46%)	(4.70%)	(8.78%)	(40.3%)	(47.2%)	(6.45%)	(29.0%)	(25.8%)	(19.3%)
SOC _{isoprene} ^b ($\mu\text{gC m}^{-3}$)	0.26	0.49	0.09	0.01	0.03	0.01	0.66	0.68	0.01	0.01	0.03	0.03
SOC _{monoterpenes}	0.30	2.18	0.09	0.06	0.05	0.05	3.41	2.57	0.04	0.50	0.54	0.08
SOC _{β-caryophyllene}	0.06	1.08	0.08	0.05	0.06	0.06	2.48	1.10	0.06	0.21	0.19	0.08
SOC _{toluene}	0.12	0.30	0.07	0.05	0.05	0.05	0.61	0.39	0.05	0.22	0.25	0.07
Total SOC	0.74	4.05	0.32	0.17	0.19	0.16	7.16	4.74	0.16	0.93	1.01	0.26
	(18.0%)	(48.4%)	(16.2%)	(6.61%)	(4.58%)	(8.90%)	(49.7%)	(59.3%)	(7.52%)	(32.6%)	(33.5%)	(19.5%)
Origin of pollution source	local	regional	local	local	local	local	regional	regional	local	local	regional	local

^a A factor of 1.9 was used to estimate the OM from local sources and 2.2 for that from regional sources.

^b SOA and SOC are the total mass concentrations of SOA and SOC produced by isoprene, monoterpene, β -caryophyllene and toluene.

^c The Teflon filter was torn on this sampling day. Therefore no PM_{2.5} mass concentration was available.

[#] SO₂ and O₃ data were not available for UST site.

Figure S1. Backward trajectories of air masses arriving Hong Kong on the regional days (Hong Kong local time = UTC + 8).

Figure S2 EI mass spectrum of the TMS-derivative of tentatively identified 2,3-dihydroxy-4-oxopentanoic acid in the derivatized extract of PM_{2.5} aerosols collected in Hong Kong.