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This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

# Composition of semi-volatile organic compounds in the urban atmosphere of Singapore: influence of biomass burning

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Received: 27 February 2010 - Accepted: 18 March 2010 - Published: 1 April 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.





### Abstract

An intensive field study was conducted in the urban atmosphere of Singapore to investigate the composition of organic compounds in both gaseous and particulate phases during the period of August to early November 2006. 17 atmospheric samples were collected. These samples were subjected to accelerated solvent extraction with a mixture of dichloromethane and acetone and separated into functional group fractions for analyses by GC/MS. Over 180 organic compounds belonging to three major fractions (n-alkanes, polycyclic aromatic hydrocarbons (PAHs), and polar organic compounds (POCs)) were identified and quantified. The characteristics and abundance of the nalkanes, PAHs, mono and dicarboxylic acids, methoxylated phenols and other POCs were determined. The composition of these organic compounds fluctuated temporally with most of them being relatively higher in October than those in other months of the sampling period. 3-D backward air mass trajectory analyses together with the carbon preference index (CPI), molecular diagnostic ratios and molecular markers were

- used to investigate the origin of organic species measured in this study. Based on these diagnostic tools, the increased abundance of atmospheric organic species during October could be attributed to the occurrence of regional smoke haze episodes due to biomass burning in Indonesia. Among the POCs investigated, phthalic acid and cis-pinonic acid showed a strong linear relationship with maximum daily ozone concen tration, indicating secondary organic aerosols (SOA) to be an important contributor to
- ambient atmospheric organics over Singapore.

### 1 Introduction

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Air pollution in Southeast Asia (SEA) is a subject of interest from both regulatory and scientific perspectives since regional emissions are growing rapidly as a result of increasing population, expanding economies, and the associated systems of energy consumption and production. The potential for trans-boundary air pollution problems in

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SEA is also great due to high emissions and the close proximity of many of the major industrial and urban centers (e.g. Bangkok, Kuala Lumpur, Singapore, and Jakarta). Regional air pollution problems such as reduced visibility and acid deposition are already apparent in the region (Balasubramanian et al., 1999, 2003; Siniarovina and Engardt, 2005; See et al., 2006). Partially because of the recurring regional haze episodes resulting from forest and peat fires, there has been an increase in the number of air guality monitoring stations in the region.

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Among air pollutants, airborne particulate matter (PM) is unique because of its potential complexity in terms of both chemical composition and physical properties. In

- order to understand the role of PM in regional air pollution and atmospheric chemistry issues, it is important to know their detailed chemical composition. A number of studies on PM compositions in SEA have been reported, but most of these studies were focused on measuring specific aerosol components (e.g. total mass, elements, organic carbon/elemental carbon (OC/EC) and water-soluble ionic and organic species over a the time to the total of the section of the sec
- <sup>15</sup> limited period of time (Ru et al., 2000; Gras et al., 1999; Nakajima et al., 1999, 1999; Radojevic and Hassan, 1999; Muraleedharan et al., 2000; Okada et al., 2001; Salam et al., 2003). We did a comprehensive characterization of atmospheric aerosols in Singapore on a daily basis for a year (Balasubramanian et al., 2003) which revealed that a significant fraction of the total mass can be attributed to organic constituents.
- <sup>20</sup> Organic matter in aerosols is composed of a large number of individual compounds and is widespread in the environment. The typical sources include natural and anthropogenic emissions such as forest fires, volcanic eruptions, incomplete combustion of fossil fuels, wood, agricultural debris or leaves, and fugitive emissions from industrial processes (Simoneit et al., 1977; Simoneit, 1984; Rogge et al., 1993; Fang et al.,
- 1999; Fraser et al., 1999; Schauer et al., 2007). PM can also be formed from nucleation of atmospheric transformation products of volatile organic compounds (VOC) or their adsorption on the surface of the pre-existing aerosol (Pandis et al., 1992; Penner and Novakov, 1996). Formation of secondary organic aerosol (SOA) has been extensively studied under simulated laboratory conditions in the last two decades (Seinfeld



and Pankow, 2003). However, data on detailed speciation of organic species in urban aerosols especially in SEA are still limited. This is probably due to analytical difficulties and the complexity of the compounds present.

- To improve our knowledge on the particulate air pollution in SEA and to address the needs for a comprehensive characterization of PM and their effects, it is necessary to have information on the detailed chemical composition of urban organic aerosols. An important aspect with regard to the atmospheric fate of organic aerosols is that semivolatile organic compounds (SVOCs) such as n-alkanes, polycyclic aromatic hydrocarbons (PAHs) and polychlroniated biphenyls (PCBs) tend to be partitioned between the gas and particle phases which could affect their transport and transformation in urban
- atmospheres. We recently studied the gas/particle partitioning of PAHs and PCBs in the tropical atmosphere of SEA based on both absorption and adsorption models (He and Balasubramanian, 2009).

In the present study, the compositions of the nonpolar and polar organic compounds in both gas and particulate phases were determined from August through early November 2006 in order to determine temporal variability. Molecular distributions and concentrations of n-alkanes, PAHs and POCs were quantified under different meteorological conditions. Based on molecular distributions of the compounds studied, potential emission sources for the atmospheric particles were assessed and suggested. This is the first detailed report of this nature for Singapore.

2 Experimental procedures

#### 2.1 Sample collection

SVOCs distributed between particulate and gaseous phases were collected from August to early November of 2006 by a high-volume sampler (Model: PUF-3300 BRL,

<sup>25</sup> HI-Q Environmental, USA) at the Atmospheric Research station with a 12 h or 24 h sampling time; this site is located on the roof of one of the tallest buildings at the Na-



tional University of Singapore campus. Singapore is located at the southern tip of the Malayan Peninsula, between latitudes 1°09′ N and 1°29′ N and longitudes 103°36′ E and 104°25′ E, and measures 42 km from East to West and 23 km North to South. The sampling site is 67 m above the sea level, and is approximately 800–1000 meters away

- from the open sea. The air quality at the sampling site is influenced by local emissions from chemical industries, major power plants, and petroleum refineries located in the southwest direction and also by urban vehicular traffic. There are two main seasons, the Northeast Monsoon from November through February and the Southwest Monsoon from July through October. These two seasons are separated by two relatively
   short intermonsoon periods, with winds blowing in no fixed direction. The months of
  - February and March are relatively drier.

Airborne particles were collected by a pre-fired quartz filter of 4 inches diameter followed by an adsorbent cartridge filled with 3 pieces of one-inch PUF plugs connected in series (7.62 cm) which were used to trap organic compounds partitioned into gas

- <sup>15</sup> phase. These filters were annealed at 450 °C for 24 h prior to use. Pre-cleaning of PUF plugs was carried out using 33 mL stainless steel vessels of a Dionex ASE 200 with the pure hexane, mixture of hexane and acetone (3:1) and pure acetone for two cycles, respectively. The high-volume PUF sampler can collect air at a rate of ca. 250 L min<sup>-1</sup>. After sampling, PUF plugs were wrapped in pre-cleaned aluminum foil and stored in
- <sup>20</sup> moisture-free and air-tight glass containers, while particulate filters were conditioned in a desiccator for 24 h, weighed, wrapped and placed with paired PUF plugs. The samples were stored -20°C before they were shipped to the collaborator's laboratory in the Department of Atmospheric Sciences at Desert Research Institute (Nevada, US) for GC-MS analysis.

### 25 2.2 Analytical methodology

A detailed description of the analytical procedure used for extraction, separation and analysis of the main organic fractions has been published elsewhere (Rinehart et al., 2006, Mazzoleni et al., 2007). Briefly, several isotopically labeled internal standards



were added to each quartz filter and PUF cartridge sample prior to extraction. Those quartz filters paired with PUF samples were extracted by accelerated solvent extraction (Dionex ASE 300 Accelerated Solvent Extrator) with dichloromethane followed by acetone; these extracts were then combined and concentrated by rotary evaporation followed by moisture-filtered ultra high purity (UHP) nitrogen blow down and then split

- followed by moisture-filtered ultra high purity (UHP) nitrogen blow down and then split into two fractions. The first fraction was analyzed without further alteration for PAHs and n-alkanes by gas chromatography coupled with mass spectrometry (GC/MS). The second fraction was evaporated to 100 μL under moisture-filtered UHP nitrogen and transferred to 300 μL silanized glass inserts. Samples were further evaporated to 50 μL and
- <sup>10</sup> 25 µL of pyridine, 25 µL of additional internal standards, and 150 µL of BSTFA with 1% TMCS [N, O-bis (trimethylsilyI) trifluoroacetamide with 1% trimethylchlorosilane] were added. These derivatizing reagents convert the polar compounds into their trimethylsilyl derivatives for analysis of organic acids, methoxyphenols, cholesterol, sitosterol, etc. The glass insert containing the sample was put into a 2 ml vial and sealed. The sample
- <sup>15</sup> was then placed into a thermal plate (custom made) containing individual vial wells at 70 °C for 3 h. The calibration solutions were freshly prepared and derivatized just prior to the analysis of each sample set, and then all samples were analyzed by GC/MS within 18 h to avoid degradation. The samples were analyzed by electron impact ionization GC/MS technique using a Varian CP-3400 gas chromatography with a model 20 CP-8400 Auto-sampler and interfaced to a Saturn 2000 Ion Trap Mass Spectrometer.
- Results are reported after blank subtraction with a composite field blank of 5 individual field blanks which were treated identically as above.

### 2.3 Airmass backward trajectory analysis

The latest, updated Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT)
 model (Version 4.9) (Draxler and Rolph, 2003; Rolph, 2003), developed by the National Oceanic and Atmospheric Administration (NOAA), was used to compute backward trajectories for air samples taken from August 2006 to November 2006. Meteorological data were obtained from National Centers for Environmental Prediction (NCEP) Global

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Data Assimilation System (GDAS, global, 2005–present). Kinematic 3-D trajectories were used as they are reported to provide an accurate description of the history of air masses in comparison with all of the other approaches (isentropic, isobaric) (Stohl, 1998; Stohl and Seibert, 1998). Backward air trajectories were generated at eight starting times per sample (every 3 h during each sampling event) for 96 h back in time with 500 m a.g.l. ending level. This atmospheric level is very frequently used (Lee et al., 2006; Erel et al., 2007) and ensures that the trajectory starts in the atmospheric boundary layer (ABL) (Dvorská et al., 2009). In addition, cluster analysis was conducted by using HYSPLIT model (version 4.9) as well to classify the trajectory groups of similar
10 length and curvature for monsoon and pre-monsoon seasons (Stohl, 1998).

### 3 Results and discussion

### 3.1 Trajectory analysis and temporal variations in TSP concentrations

The 96 h backward trajectories of air masses arriving at the study site during this sampling period were computed and are categorized in Fig. 1.

- Cluster 1 a category of air masses representative of Southwest monsoon season (August–September 2006). This category accounted for 98.6% of all the air masses received at the sampling site during the SW monsoon. The air quality in Singapore was partially influenced by the air masses transported from Indonesia, and few hotspots (forest and peat fires) were observed in Sumatra and Kalimantan during this period as evident from satellite images (National Environment Agency (NEA), Singapore).
  - 2. Cluster 2 a category of air masses for October 2006. The pre-northeast monsoon, characterized by relatively low wind speeds, is usually experienced in the month of October. However, the air mass sources were still the same as those in August and September 2006, with 89.7% of air masses originating from the



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Southwest sector. These air masses were partly terrestrial and partly oceanic in origin, passing through islands of Southern Indonesia such as Sumba, Lombok and Sumbawa, Java Sea, mass islands of Java and Southwestern Sumatra, and in some cases crossing Kalimantan (Borneo) Island before arriving at Singapore. Notably, the number of dense hotspots detected in Sumatra and Borneo increased significantly during this month (representative hotspot map in Fig. 1d).

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3. Cluster 3 – a category of air masses during early November 2006. 100% of air masses received at the site came from the Northeast (NE) areas (Fig. 1c). Most of air masses sampled were of oceanic character, travelling over the South China Sea; some originated from the Southern China such as Hainan, Canton provinces or Taiwan Island/strait as well. The air quality in Singapore was influenced by cleaner air masses of oceanic origin following their long-range transport from NE direction.

Figure 2 shows the daily average concentrations of total suspended particles (TSP)
and Pollution Standard Index (PSI) readings which are indicative of ambient air quality. An index value of 1 to 50 indicates that the air quality is in the good range for that day, 51 to 100 in the moderate range and a value of >100 would mean that the air quality is unhealthy (NEA). As can be seen from Fig. 2, both the PSI and the TSP concentrations tracked each other reasonably well during this sampling period, suggesting that the PSI for the day was determined by the prevailing TSP concentrations. It could also be seen that there was a sporadic increase in the values of both the PSI (maximum 150) and

- that there was a sporadic increase in the values of both the PSI (maximum 150) and the TSP (maxium 273.4  $\mu$ g m<sup>-3</sup>) on a number of occasions during October which was presumably due to the influence of biomass burning-impacted air masses advected from Indonesia (Fig. 1b). As a result of the onset of the inter-monsoon season in early
- <sup>25</sup> November, relatively cleaner oceanic air masses blew into Singapore (Fig. 1c), leading to a significant improvement in air quality as reflected by the PSI and TSP values.

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### 3.2 Aliphatic Hydrocarbons (AH)

The measurement of the homologous series n-alkanes in the hydrocarbon fraction of the air samples allowed the determination of their occurrence, relative distribution, CPI, C<sub>max</sub> (carbon number maximum), and wax n-alkanes (WNA) content as shown in Table 1. The monthly average concentrations (particulate plus gas) of AH were

 $66.13\pm11.04$ ,  $45.32\pm2.91$ ,  $801.34\pm443.9$  6 and  $71.20\pm21.56$  ng m<sup>-3</sup> during August, September, October and Novemeber 2006, respectively.

The relative distributions of the n-alkanes mainly ranged from C<sub>12</sub> to C<sub>35</sub> (some of the representative distributions are shown in Fig. 3). It has been reported that a C<sub>max</sub>
 between 27–33 is characteristic of biogenic sources (higher plant wax) while a C<sub>max</sub> at lower carbon numbers may indicate a major input from petrogenic source (Gogou et al., 1996; Abas et al., 2004). In this study, the C<sub>max</sub> was at C<sub>21</sub> or C<sub>22</sub> for Aug and Sept samples, with monomodal distributions at low carbon numbers which is characteristic

- of dominant petrogenic sources, mostly from local urban emissions. However, during the first and third weeks of October, the  $C_{max}$  increased to  $C_{31}$  (e.g. 7–8 October, 16– 17 October 2006, Fig. 3) with peaks in both TSP and PSI values (Fig. 2), implying a higher contribution from biogenic inputs for n-alkanes. The shift in the  $C_{max}$  to a higher carbon number could be attributed to the transport of biomass burning-impacted air masses from Indonesia (see Fig. 1) where more organic components could be emitted
- from the epicuticular waxes of vascular plants and from direct suspension of pollen and microorganisms (Yassaa et al., 2001). In addition, the C<sub>max</sub> diverged with bi-modal distributions of n-alkanes for those samples collected in the second week of October (e.g. 13–14 October 2006, Fig. 3). Early in November, the abundance of n-alkanes decreased to 71.20±21.56 ng m<sup>-3</sup> but C<sub>max</sub> was still centered at C<sub>31</sub>(e.g. 2–4 November, 9–11 November 2006, Fig. 3), indicating that residual amounts of n-alkanes of biomass.
- <sup>25</sup> 9–11 November 2006, Fig. 3), indicating that residual amounts of n-alkanes of biomass burning origin possibly still existed on a regional scale.

The CPI which expresses the ratio of odd-carbon-numbered to even-carbonnumbered n-alkanes in a given sample has been used to differentiate biogenic n-

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alkanes from those of petrogenic or anthropogenic origin (Simoneit and Mazurek, 1982; Simoneit, 1989; Zheng et al., 2000; Bi et al., 2002; Young, 2002). In general, CPI values >2 indicate predominant biogenic sources such as epicuticular waxes of terrestrial plants, and CPI values of near unity signify the source of fossil fuels or incomplete combustion of petroleum products (Simoneit, 1984; Wu et al., 2005). The average CPI values for the entire range (CPI<sub>1</sub>), petrogenic (CPI<sub>2</sub>) and biogenic (CPI<sub>3</sub>) for those samples collected during August, September and November 2006 were lower than those during October (Table 1). Although the influence of anthropogenic activities such as fossil fuel combustion, petroleum and diesel residues on the local air quality was evident from the CPI values (<2), the contribution of biomass burning-related sources to

dent from the CPI values (<2), the contribution of biomass burning-related sources to the increased abundance of atmospheric organic compounds in October is particularly noteworthy.

Since n-alkanes derived from fossil or petroleum sources have CPI close to 1, the residual plant wax n-alkanes could be separated from fossil components by subtracting the corresponding n-alkane concentrations of CPI close to 1 (Simoneit, 1989; Simoneit et al., 1991). The plant wax alkanes can be estimated through the following equation (Simoneit et al., 1991):

 $WaxC_n = [C_n] - [(C_{n+1} + C_{n-1})/2]$ 

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The highest plant wax n-alkanes input (WNA) with  $35.75\pm3.58\%$  was observed during October; the atmospheric samples collected during the months of August, September and November 2006 showed the plant wax n-alkanes inputs of  $10.88\pm4.89\%$ ,  $6.72\pm3.77\%$  and  $15.16\pm3.69\%$ , respectively. A strong linear relationship ( $R^2$ =0.98) between WNA% and CPI<sub>1</sub> was observed as shown in Fig. 4. This correlation was higher than those reported for other urban areas such as Guangzhou of China ( $R^2$ =0.91) (Wu et al., 2005) and Greece ( $R^2$ =0.95) (Gogou et al., 1996), indicating that the CPI and %WNA could be used in the source assignments of atmospheric organic compounds

including those in both the particulate and gaseous phases.



(1)

### 3.3 Polycyclic aromatic hydrocarbons

The levels of 93 PAH compounds including non-alkylated, methyl-alkylated, and oxygenated PAHs determined in this study is given in the Supplemental Table S1 (http://www.atmos-chem-phys-discuss.net/10/8415/2010/acpd-10-8415-2010-supplement.

pdf). The occurrence levels of PAHs during August, September and November 2006 were relatively lower than those in October. From 10 to 14 October, air samples were collected for 12 h (daytime and nighttime). The presence of non-alkylated and methyl-alkylated PAHs in the nighttime were 2~3 times higher that in the daytime, which might be due to their degradation (photooxidation processes) in the daytime during the dry, oxidative environmental conditions of this period coupled with low wind speeds. This may also be due to different meteorological conditions during day and night, for example, lower inversion layer at night.

Since PAHs are produced and emitted through incomplete combustion processes such as biomass combustion, vehicular and industrial emissions, most of the PAHs

- <sup>15</sup> cannot be used as exclusive markers for biomass combustion such as peat and forest fires. Among the PAHs identified in this study, 1-methyl-7-isopropylphenanthrene (retene) has been reported to be a molecular tracer compound for coniferous wood combustion which is formed by thermal degradation of resin compounds in the wood (Ramdahl, 1983; Standley and Simoneit, 1994; Oros and Simoneit, 2001). During <sup>20</sup> most of the sampling period, retene was either non-detectable or existed with very low concentrations (2~7 pg m<sup>-3</sup>). However, its concentration was significantly higher in the month of October with its range between 6~73 pg m<sup>-3</sup> and showed a moderate positive correlation with total PAHs with the  $R^2$  of 0.52 (Fig. 5). This observation suggests that the atmospheric composition of organic compounds was influenced by long-distant
- <sup>25</sup> pyrogenic (biomass combustion) sources in Indonesia.

PAH concentration ratios have been widely used to identify combustion-derived PAHs (Benner et al., 1995; Yunker et al., 1996; Budzinski et al., 1997). In order to assess their potential sources in this study, a variety of PAH ratios were calculated for all air sam-

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ples as listed in Table 1. It has been reported that fluoranthane/fluoranthane+pyrene (Flt/Flt+Pyr) ratios below 0.40 imply the contribution of unburned petroleum (petrogenic sources) and ratios between 0.40 to 0.50 suggest their emissions from the combustion of liquid fossil fuels (vehicle and crude oil), whereas ratios larger than 0.50 are characteristic of grass, wood, or coal combustion (Yunker, 2002). In addition, it has been suggested that indeno(1,2,3-cd)pyrene/indeno(1,2,3-cd)pyrene+benzo(q,h,i)perylene (Ind/Ind+B(ghi)P) ratios lower than 0.20 likely imply petroleum emissions, ratios between 0.20 and 0.50 imply liquid fossil fuel combustion and those greater than 0.50 are indicative of grass, wood and coal combustion (Yunker, 2002). In this study, both of these two ratios were between 0.30 and 0.48 for those samples collected during the 10 months of August, September and November, suggesting the dominant contributions of local sources of PAHs such as emissions from on-road vehicles and petroleum industry in general. However, for samples collected in October 2006, these ratios were slightly greater than 0.50, indicating biomass/peat combustion in Indonesia might contribute relatively more to the PAHs measured during this period. The relative abundance of 15  $C_0$  to  $C_1$  alkyl-PAH homologues ( $C_1$ -178 and 202 isomers) has also been used to distinguish between petroleum and combustion emissions, among which  $C_0/C_0+C_1$  P/A (ratio of phenanthrene plus anthracene to phenanthrene plus anthracene plus C1-178

- isomers) and  $C_0/C_0+C_1$  F/P (ratio of fluoranthene plus pyrene to fluoranthene plus pyrene plus  $C_1$ -202 isomers) were applied in this study (Gogou et al., 1996; Budzinski et al., 1997; Simo et al., 1997). In general, environmental samples with  $C_0/C_0+C_1$  F/P or  $C_0/C_0+C_1$  P/A below 0.5 supposedly indicate petroleum sources, while ratios higher than 0.50 are indicative of combustion emissions (Yunker, 2002). The average ratio of  $C_0/C_0+C_1$  F/P, a better indicator of combustion sources other than petroleum (Yunker
- et al., 2002), was particularly higher (>0.5) for the air samples collected in the month of October as compared to those for other months (Table 1), implying higher PAHs measured during this sampling duration could be due to regional combustion sources such as biomass and peat combustion.

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It should be noted that PAH diagnostic ratios have some limitations for source assignments as stated by Galarneau (2008) due to various factors such as substantial intra-source variability and inter-source similarity of PAH isomer ratios, variations in PAH concentrations because of gas/particle partitioning, precipitation scavenging, par-

- ticle deposition, etc. However, considering the fact that Singapore is a small but highly industrialized country with no distinct seasons in a year, there is little variation of atmospheric temperatures leading to relatively consistent gas/particle partitioning processes throughout the year. In this study, the effect of gas/particle partitioning variations on PAH diagnostic ratios was overcome by calculating diagnostic ratios of total PAH con-
- <sup>10</sup> centrations (gas plus particles). As reported by He and Balasubramanian (2008), organic compounds with more volatility tend to be redistributed onto larger particles while the less volatile compounds remain onto the fine particles with which they were directly emitted from their corresponding sources. From this distribution pattern, it is reasonable to assume that the compounds with similar volatility (LMW or HMW) may have
- similar particle scavenging efficiency by precipitation or similar dry deposition as the particle size distribution of PAH species is a major factor affecting the efficiency of the above-mentioned atmospheric removal processes. Based on these considerations, we hypothesize that the molecular diagnostic ratios of PAHs used in this study provide some insights into the temporal variations of their source profiles.

#### 20 **3.4** Polar organic compounds

A total of 63 polar organic compounds from both particulate and gaseous samples were detected as reported in a Supplemental Table S1 (http://www. atmos-chem-phys-discuss.net/10/8415/2010/acpd-10-8415-2010-supplement.pdf), which include alkanoic acids, n-alkanedioic acids, aromatic carboxylic acids and methoxylated phenols (Table 1).

N-alkanoic acids ranged from  $C_{10}$  to  $C_{24}$  with a strong even carbon number predominance with total monthly concentrations ranging from 27.48 to 467.58 ng m<sup>-3</sup> and with CPI between 0.46 and 4.63. During the sampling period with the exception of the



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month of October, myristic acid ( $C_{14}$ ) was the most abundant species in most of the composites, followed by palmitic acid ( $C_{16}$ ), which was presumably contributed by microbial activities and urban emissions (Simoneit and Mazurek, 1982; Simoneit, 1984). However, in October 2006,  $C_{max}$  was centered at  $C_{21}$  and  $C_{23}$ , suggesting possible influence from biomass combustion sources of aerosols (Simoneit, 1984).

A series of alkanedioic acids were present in atmospheric samples, ranging from  $C_4$  to  $C_{14}$  (Supplemental Table S1 http://www.atmos-chem-phys-discuss.net/10/8415/2010/acpd-10-8415-2010-supplement.pdf). The alkanedioic acids could originate from a variety of sources in the environment. The  $C_5$  and  $C_6$  homologues are formed by the oxidation of cyclic olefins (Hatakeyama et al., 1985), while  $C_8$  and  $C_9$  ones are formed by the photo-oxidation of unsaturated carboxylic acids such as oleic ( $C_{18:1}$ ) and linoleic acids( $C_{18:2}$ ) (Stephanou, 1993a). As can be seen from Table S1, succinic acid (C4) was predominant in most of the samples with unimodal GC chromatograph. This finding is consistent with earlier reports in the literature that succinic acid was the most

<sup>15</sup> abundant alkanedioic acid in most of the urban atmosphere and was attributed to both vehicular emissions and biomass combustion (Kawamura, 1987; Rogge, 1998). The distribution of dicarboxylic acids was bimodal in the atmospheric samples collected during October, with the  $C_{max}$  located at  $C_4$  and  $C_{10-12}$ . High molecular weight alkanedioic acids ( $n > C_{10}$ ) have been identified in rural aerosol particles and their source might be oxidation products of hydroxyl alkanoic acids from polyester biopolymer (Simoneit and Mazurek, 1982).

Anhydrosugars such as levoglucosan are known to be emitted from biomass burning (Abas et al., 2004; linuma et al., 2007; Simoneit, 2007; Simoneit et al., 1999). As can be seen from Fig. 7, the temporal trends of levoglucosan and TSP are quite similar during the entire sampling period with significant correlation (0.64) at the 0.01 level (2-tailed); for those samples collected in October 2006, the correlation between levoglucosan and TSP was even more significant (0.76 at 0.002 level (2-tailed)). However, the concentration of levoglucosan measured in this study during the biomass burning period was relatively lower than those reported in other biomass burning-advected

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air masses from elsewhere (Muhle et al., 2007; Stohl et al., 2006; Ward et al., 2006; Leithead et al., 2006; Medeiros et al., 2006). The reported bulk emission factors of levoglucosan from wood combustion vary widely ranging from 0.42 mg kg<sup>-1</sup> for western white pine (Oros and Simoneit, 2001) to 1900 mg kg<sup>-1</sup> for eucalyptus (Schauer et al., 2001). Likewise, emissions of levoglucosan from controlled biomass burning experiments under laboratory conditions also showed large variations depending on the type of stoves used, biofuel qualities and operating conditions (Hedberg et al., 2006, Mazzoleni et al., 2007). The emission factors of levoglucosan from different types of vegetation and peat fires in Indonesia remain unknown. Furthermore, levoglucosan
<sup>10</sup> was probably incorporated into primary particles which might have undergone dry deposition from the atmosphere following their hygroscopic growth during the course of long-range transport from Indonesia to Singapore.

Substituted phenols, the lignin decomposition products as phenols with methoxy groups attached on the aromatic rings, were investigated in this study as well (Si-<sup>15</sup> moneit, 2002; linuma et al., 2007). Vanillin, 3-hydroxy-4-methoxybenzoic acid, was found to be most pronounced in this group of organic compounds with a peak occurrence (19.16 ng m<sup>-3</sup>) on 7–8 October 2006, which suggests vanillin emissions from biomass and peat combustion (linuma et al., 2007).

Among other polar organic compounds, both cis-3-acetyl-2,2-dimethyl cyclobutaneacetic acid (cis-pinonic acid) and 1,2-benzenedicarboxylic acid (phthalic acid) merit special attention as they have been identified as photochemical products in smog chamber experiments and proposed as surrogates for the contribution of secondary organic aerosols (SOA) to ambient samples (Lee and Kamens, 2005; Ray and Mcdow, 2005; Park et al., 2006; Na et al., 2007). Cis-pinonic acid is one of the  $\alpha$ -pinene oxidation products (Park et al., 2006) while phthalic acid is a product of naphthalene photodegradation (Bunce et al., 1997) and possibly photodegradation of other polycyclic aromatic hydrocarbons in atmospheric aerosols (Jang and McDow, 1997). The formation of these organic acids through atmospheric oxidation could be partially explored by comparing concentration trends between these compounds and ozone as

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shown in Fig. 6. Moderately strong linear relationships ( $R^2 = 0.52 \sim 0.76$ ) were obtained for all sampling periods, indicating the likelihood that phthalic acid, cis-pinonic acid and ozone could be the products of the same atmospheric oxidation processes. Alternatively, these two organic acids might serve as indicators of photochemical activity leading to SOA in this region.

#### 4 Conclusions

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The molecular composition of organic compounds present in both gaseous and particulate atmospheric samples collected in Singapore from August to early November 2006 has been determined by GC-MS. In this study, a total of 17 samples were analyzed for over 180 organic compounds grouped into three major fractions (n-alkanes, 10 PAHs and POCs). As for n-alkanes, the C<sub>max</sub> shifted from C<sub>20</sub>-C<sub>22</sub> during August-September 2006 to  $C_{31}$  or bi-modal distributions at  $C_{21}$  and  $C_{31}$  in October 2006, indicating that organic pollutants in August-September 2006 samples were of dominant petrogenic signatures, while those from October 2006 were derived from vascular plant wax alkane inputs. In addition, the CPI values (CPI<sub>1</sub>, CPI<sub>2</sub>, CPI<sub>3</sub>) increased from 15  $1.15 \pm 0.14$ ,  $1.17 \pm 0.19$ ,  $1.44 \pm 0.29$  before October to  $1.59 \pm 0.10$ ,  $1.88 \pm 0.26$ ,  $1.77 \pm 0.18$ during October 2006. On the average, 35.7% of n-alkanes came from biomass burning during October 2006; in contrast, only 9.6% of alkanes were of biomass burning origin from August to September 2006. The influence of biomass burning on the regional air quality is supported by the general increasing tendency of PAH diagnostic ratios 20 during October 2006 as compared to those investigated in other months. Among the polar organic compounds, which were converted to their trimethylsilyl derivatives and

polar organic compounds, which were converted to their trimethylsilyi derivatives and measured by GC/MS, organic acids were the most abundant group detected in almost all samples, followed by methoxyphenols and sterols, etc. Our results suggest that
 the contribution of biomass burning inputs to the observed abundance of atmospheric organic compounds in Singapore during October 2006 was significant as compared to those found in other months of the sampling period.

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Acknowledgement. One of the authors, Rajasekhar Balasubramanian, gratefully acknowledges the support from the Singapore-Delft Water Alliance (SDWA). The research presented in this work was carried out as part of the SDWA's research programme (R-264-001-013-272).

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Compound classes (ng m $^{-3}$ )	Aug 2006	Sep 2006	Oct 2006	Nov 2006
n-alkanes				
Total concentration	66.13±11.04	45.32±2.91	801.34±443.96	71.20±21.56
Homologues range		C <sub>12</sub>	2-C <sub>35</sub>	
<i>C</i> <sub>n</sub> max	C <sub>21</sub>	C <sub>21</sub> , C <sub>22</sub>	C <sub>21</sub> , C <sub>31</sub>	C <sub>31</sub>
CPI <sub>1</sub>	1.20±0.21	1.11±0.07	$1.59 \pm 0.10$	1.23±0.13
CPI <sub>2</sub>	1.27±0.14	1.06±0.23	1.88±0.26	1.56±0.32
CPI <sub>3</sub>	1.48±0.44	1.39±0.23	1.77±0.18	1.41±0.13
WNA (%)	10.88±4.89	6.72±3.77	35.75±3.58	15.16±3.69
PAHs				
Non-alkylated	10.08±3.89	10.58±1.48	16.33±10.63	4.50±2.61
Methyl-alkylated	8.71±4.65	4.60±1.06	13.78±8.14	4.93±0.74
Oxygenated	3.06±0.23	1.90±0.66	9.65±3.74	4.14±1.42
Others	0.60±0.42	0.15±0.16	1.52±1.54	0.21±0.26
Flt/(Flt+Pyr)	0.44±0.05	0.44±0.03	0.52±0.02	0.48±0.11
Ind/(Ind+B(ghi)P)	0.35±0.02	0.35±0.04	0.54±0.11	0.43±0.08
$C_0/(C_0+C_1) P/A$	0.44±0.02	0.34±0.12	0.52±0.10	0.48±0.06
$C_0/(C_0+C_1)$ F/P	$0.56 \pm 0.05$	0.53±0.08	$0.80 \pm 0.05$	0.65±0.07
Polar compounds				
n-Alkanoic acids	96.97±1.05	95.48±6.11	301.56±132.44	135.21±10.57
CPI for n-alkanoic acids	0.98±0.56	$1.30 \pm 0.42$	3.52±1.37	1.57±0.97
n-Alkanedioic acids	83.12±6.92	54.22±18.96	217.22±40.76	86.02±23.28
Methyl-alkanedioic acids	23.02±8.47	9.73±3.76	70.31± 46.70	5.97±2.41
Anhydrosugar (levoglucosan)	6.11±0.98	4.45±0.78	9.31±2.81	$3.32 \pm 0.44$
Aromatic monocarboxylic acids	190.96±58.70	134.80±15.32	316.43±125.72	$73.60 \pm 29.35$
Aromatic dicarboxylic acids	6.82±3.65	5.02±2.91	18.38±3.98	9.84±4.70
Methoxylated phenols	0.95±0.12	1.31±0.31	6.40±9.28	2.27±0.90
Others	20.97±11.02	13.49±2.26	52.65±20.46	24.19±15.45
Total concentration of	514.16±110.86	379.56±56.59	1831.47±658.1	425.69±113.54
all organic compounds				

**Table 1.** Organic compounds characteristics of air samples of 2006 over Singapore (ng  $m^{-3}$ ).

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**Fig. 1.** Air mass backward trajectories from August to early November of 2006 in Singapore and the representative distribution of hotspots in SEA in Oct 2006 (a) Cluster 1 (August–September 2006); (b) Cluster 2 (October 2006); (c) Cluster 3 (November 2006); (d) Hotspot map on 14 October 2006.

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**Fig. 2.** Temporal Changes in Total Suspended Particulate matter (TSP) concentrations and Pollutants Standard Index (PSI) from August to October 2006.

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Fig. 3. Distributions of n-alkanes from August to November 2006.

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Fig. 4. Correlation of % plant wax alkane and CPI<sub>1</sub>.

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Fig. 5. Correlation between retene and total PAHs.

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**Fig. 6.** Correlations between phthalic acid, cis-pinonic acid and ozone. (phthalic acid;  $\Delta$  cis-pinonic acid; (a) August, September, November 2006; (b) October 2006).



Fig. 7. Temporal trend of levoglucosan and TSP from August to October 2006.

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