

Review report (acpd-10-8415-2010)

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

General comments:

The authors report the composition of over 180 organic compounds in aerosols collected in the period of August to November 2006 in Singapore and discuss the influence of biomass burning on the organic compound composition. The data is valuable to understanding PM in Singapore and its surrounding regions. A few statements made in the abstract/conclusion are not supported with data or with analysis (see specific comments). Another concern is the unusually low levoglucosan concentrations reported in their samples, even in those influenced by biomass burning. More analytical details and comparison with measurements in the literature are needed to defend their levoglucosan data.

The authors mention in the manuscript a supporting document (<http://www.atmos-chem-phys-discuss.net/10/8415/2010/acpd-10-8415-2010-supplement.5.pdf>). I was not able to locate the document. Therefore, the comments below are made without the knowledge of the information provided in the supporting document.

Specific comments

1. Abstract:

“Among the POCs investigated, phthalic acid and cis-pinonic acid showed a strong linear relationship with maximum daily ozone concentration, indicating secondary organic aerosols (SOA) to be an important contributor to ambient atmospheric organics over Singapore.” This causal relationship is not valid. The observed correlation of phthalic acid, pinonic acid with O₃ daily maximum can only confirm the secondary nature of the two POCs. The abundance of SOA can not be deduced from the abundance of the two SOA compounds, nor can be deduced from their relationships with O₃. Therefore, the statement made in the 2nd half of the sentence does not have any supporting basis.

2. Sample collection:

More details are needed about the samples collected. I suggest that the authors add a table showing the sample details (individual sampling dates, sampling duration, temperature, PSI, TSP levels on the sampling dates). Such a table will help readers follow the discussion. (1) A total of 17 pairs of filter/PUF samples were collected for this study. This information on the number of samples was mentioned in the conclusion section. It should be clearly indicated in the introduction section. That's where readers expect to find this information. (2) The information from Figure 6 indicates a total of 20 samples (7 samples collected in the months of August, September, and November while 13 samples collected in October). Information from Figure 7 indicates a total of 19 samples collected from August to November. Please explain the discrepancy in the total number of samples. (3) The October samples were collected for shorter duration, giving day samples and night samples. Again this information is buried in the text (page 8425, line 6-7). It should be given in the experimental section. (4) I suggest indicating the 17 individual sampling days in Figure 2, which shows the temporal variation of TSP and PSI.

3. Page 8428, line 13-15: “This finding is consistent with earlier reports in the literature that succinic acid was the most abundant alkanedioic acid in most of the urban atmosphere...” This statement is incorrect. Oxalic acid is typically the most abundant dicarboxylic acid in both urban and rural atmospheres. The authors can check papers by Kawamura and coworkers to verify the relative abundance of oxalic acid and succinic acid.

4. Pages 8428-8429: The range of levoglucosan concentrations as seen in Fig. 7 was ~2 – 14 ng m⁻³. Even during the period influenced by biomass burning (i.e., October), the concentrations were

fairly low (5-15 ng m⁻³). The authors also concede that their levoglucosan concentrations were lower than those reported in the literature. If we take a few examples of levoglucosan measurements in the literature, suspicion is raised on the analytical reliability of levoglucosan. Kourtchev et al (2008, chemosphere) reported a median levoglucosan concentration of 30 ng/m³ in PM_{2.5} from a mixed forest site in western Germany; Zhang T. et al (AE, 2008) reported monthly average levoglucosan in Beijing in the period of July 2002 to July 2003 ranged from 108 to 806 ng/m³; Kumagai K. et al (2010, Aerosol and Air quality Research) measured levoglucosan in fine particles in the Kanto Plain, Japan and reported a mean concentration of 54.8 ng/m³ in spring, 37.4 mg/m³ in summer, and 258 ng/m³ in winter.

Related to the unusually low levoglucosan concentrations, the authors need to give a detailed account of their analytical QA/QC on levoglucosan to defend their data. A more thorough comparison with measurements in the literature will help to assess whether the levoglucosan concentration level reported in this work was reasonable.

5. Considering the emphasis of this manuscript is partially on influence of biomass burning on organic aerosol composition in Singapore, I suggest that the authors devote one section to discussing in detail the known biomass burning organic tracer compounds, such as levoglucosan, methoxylated phenols, and retene. A table listing the concentrations of these tracer compounds in individual samples will also help the discussion.
6. Table 1: The authors need to specify whether this table summarizes only particle-phase concentrations or the combined concentrations of gas and particle phases.
7. Conclusions (Page 8430):
“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.” This conclusion is not elaborated in the manuscript text. It appears that the authors regard plant wax n-alkanes input (WNA) (its calculation is shown on page 8424) to be entirely generated by biomass burning. There could be other sources to WNA, such as vegetative detritus generated through wind abrasion. There was no discussion on how WNA could be simply regarded to be of biomass burning origin.
8. Page 8424, lines 5-8: The carbon range for CPI₂ and CPI₃ need to be defined.
9. Page 8426, discussion of C₀/C₀+C₁ P/A and C₀/C₀+C₁ F/P: I suggest replacing the expression of the two ratios with C₀/C₀₊₁_MW178 and C₀/C₀₊₁_MW202. The expressions adopted by the authors are less direct and make it rather difficult for readers to link with the underlying meaning.
10. Page 8428, line 13: What is “unimodal GC chromatograph”?
11. Page 8429, lines 24-25: “Cis-pinonic acid is one of the α-pinene oxidation products (Park et al., 2006) ...” The reference Park et al is a study on chemical characterization of ambient PM_{2.5} organic aerosol, which does not present conclusion evidence to indicate pinonic acid is an oxidation product of α-pinene. More appropriate references are chamber studies of α-pinene (e.g., Jang and Kamen, AE, 1999; Yu et al., J. Atmos. Chem., 1999, v34, 207-258; Larsen et al., 2001, v38, 231-276).

Minor comments

Page 8426: (Yunker, 2002) appears at a few places on this page. It should be (Yunker et al., 2002).

Page 8428, line 29: biomass burning-advected → biomass burning-affected?

Fig. 7 caption: replace “October” with “November”; replace “ug” with “μg” in the y-axis for TSP.