

Responses to Referee #2

General comments:

The work reports quantification of 155 individual organic compounds in twelve compound classes in 49 PM10 samples collected in a tropical location in India. Some of the quantified compounds serve as aerosol source markers. This information is used by the authors to infer source contributions by biomass burning, plastic burning, and fossil fuel combustion. Data in this work adds to the increasing database of aerosol organic speciation; however, the authors only reported part of organic aerosol characterization results in this manuscript, making this work appear to be fragmented. They also unnecessarily limit themselves to the 155 compounds reported here in their data interpretation. More detailed comments are given below.

Response: The authors are grateful to the reviewer's comments and suggestions on this manuscript. We will combine this paper and the Fu et al., 2009b paper together. However, the Pavuluri et al., 2009a paper, which was mainly focused on the dicarboxylic acids measured by gas chromatography-flame ionization detector (GC-FID) technique, is not available because it has been accepted for publication in JGR-Atmospheres (Pavuluri et al., 2010). We will cite major conclusions of Pavuluri et al., (2010) to better characterize the organic aerosols from Southeast India. The revised manuscript will contain 14 compound classes (174 organic species) including biogenic secondary organic aerosol (SOA) tracers from the oxidation of isoprene, α/β -pinene and β -caryophyllene. To the best of the authors' knowledge, this is the first time that the SOA tracers were measured in ambient aerosols in India. All the tables and figures will be modified accordingly in the revised manuscript. In addition, we will add one new author who contributed to the work on the biogenic SOA tracers in the revised manuscript.

Specefic comments:

(1) From the information given in the manuscript, in addition to this ACP manuscript, at least two more papers report data derived from the same set of 49 aerosol samples. The two papers are: Fu, P., Kawamura, K., Pavuluri, C. M., Chen, J., and Swaminathan, T.: Molecular characterization of urban organic aerosol in tropical India: Contribution of biogenic photooxidation and source apportionment, in preparation, 2009b.

Pavuluri, C. M., Kawamura, K., and Swaminathan, T.: Water-soluble organic carbon, dicarboxylic acids, ketoacids and α -dicarbonyl in tropical Indian aerosols, J. Geophys. Res. Atmos., revised, 2009a.

As the authors explained in page 21672, the Fu et al paper (referred Fu 2009b paper below) reports biogenic SOA tracers while the Pavuluri et al paper reports low molecular weight dicarboxylic acids and hydroxyl-/polyacids. All the three papers are on organic aerosol characterization and implications for sources of organic aerosols. With the closely related information scattered in three papers, I feel this hampers the understanding of the overall picture on the organic aerosol characterization and how this molecular speciation work helps to elucidate source contributions. At the least, this paper and the Fu 2009b paper should be combined, focusing on using the whole suite of measured organic compounds for aerosol source analysis.

In my view, description of individual compound classes in sections 3.7-3.9 mainly provides trivial

information on abundance of these compounds in this study and abundance comparison with measurements made in other locations. Much of the content in these sections is better presented as supplementary information. Removal of these sections also makes room for inclusion of the important results that the authors plan to present in the Fu 2009b paper.

Response: As mentioned above, we will combine the Fu et al., 2009b paper in the revised manuscript. Although the removal of sections 3.7-3.9 was suggested by the reviewer, we believe these sections are important. Thus, we want to keep them in the main text. Especially, a good correlation was found between 1,3,5-triphenylbenzene and terephthalic acid in ambient aerosols for the first time, which suggests that terephthalic acid can be produced by the burning of plastics. This finding is very interesting because terephthalic acid was generally considered as a photooxidation products in the atmosphere.

(2) The authors' group appears to have done a comprehensive characterization of the 49 aerosol samples, including inorganic ion components (which seem to be planned to be presented in another paper, Pavuluri et al, 2009b). However, they have not fully utilized the whole range of compounds quantified using various techniques. Example 1: on the discussion of biomass burning source, it is relevant to compare the organic tracers for biomass burning aerosols with K^+ , a known inorganic tracer for biomass burning. Example 2: land-sea breeze has been proposed to be responsible for the observed diurnal pattern of higher during the nights and lower during the days for many of the quantified organic compounds. If the authors can show the diurnal gradient in Na in the aerosol samples, that would give more support to the suggestion of the dominant role of land/see breeze on the diurnal variation of the organic compounds. Example 3: in the PCA analysis of sugar compounds, some components are suggested to be related to biological substance derived from surface soil. Inclusion of Ca^{2+} will help the identification of this soil-related source, but the authors unnecessarily limited themselves to the data reported in this manuscript alone.

Response: Thanks. For Example 1, we found that there was no strong correlation ($R^2 = 0.12$) between the concentrations of levoglucosan and non-sea-salt K^+ (nss-K) in all the samples (see Figure 1), which suggests that nss-K is not a good biomass burning tracer in Chennai. Rather, we consider that cow-dung burning is an important source of levoglucosan in tropical India. The burning of cow-dung is not an “emitter” of nss-K.

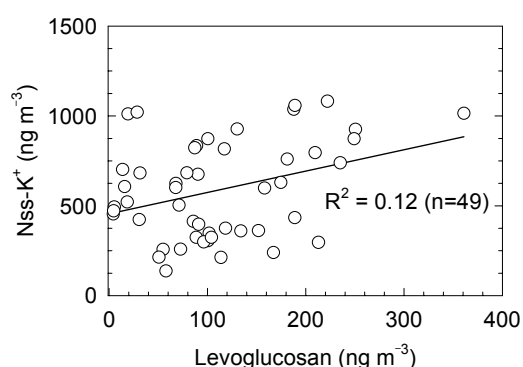


Figure 1. Relation between levoglucosan and non-sea-salt potassium (nss-K) in the Chennai aerosols.

When considering the winter and summer season respectively, the correlation coefficients (R^2) between levoglucosan and nss-K were 0.36 for winter samples ($n = 29$) versus 0.10 for summer samples ($n = 20$). Such a weak positive correlation found in winter was supported by the fact that the

air masses mainly originated from North India and Southeast Asia. In North India, the burning of wood for heating is common in winter. As discussed in the submitted manuscript, biomass burning activities in Southeast Asia are very active during dry season. We will briefly discuss these points in the revised manuscript.

Example 2: The temporal variations of Na (see Figure 2) showed that there was no clear diurnal pattern for the Chennai aerosols. Higher concentrations of Na during daytime were occasionally observed on Jan. 28, Jan 29, Feb. 2, and Feb. 5. However, previous studies have reported that a diurnal pattern of the wind in Chennai, which is located on the coast, is caused by land-sea breeze in all seasons (Srinivas et al., 2007; Venkatesan et al., 2009). During sampling period in the present study, the wind is southwesterly (land-breeze) during early hours of the day (Pavuluri et al., 2010). However, it turns northeasterly and southeasterly at noon hours (12:00-13:00 LT) during both winter and summer, and accelerates subsequently as a result of the onset of sea breeze. The sea breeze may continue until late night (Venkatesan et al., 2009) but its strength vary with the changes in wind speed. We will add this information in the revised manuscript.

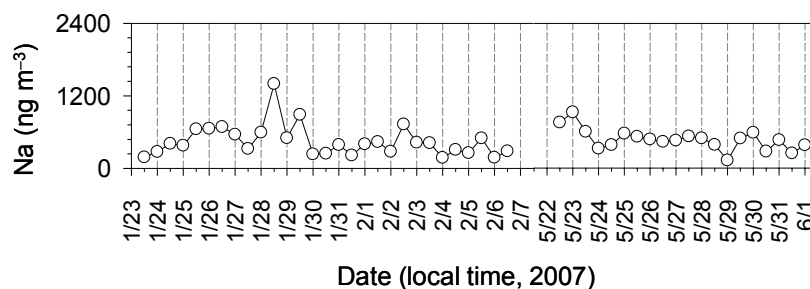


Figure 2. Temporal variations of Na in the Chennai aerosols.

Example 3: As suggested by the reviewer, we found good correlations between nss-Ca and sugar compounds such as sucrose and trehalose during both wintertime and summertime (see Figure 3), which further support the idea that these compounds may partly originate from soil resuspension. We will add this information in the revised manuscript and keep the PCA analysis results (Table 2) as published in ACPD.

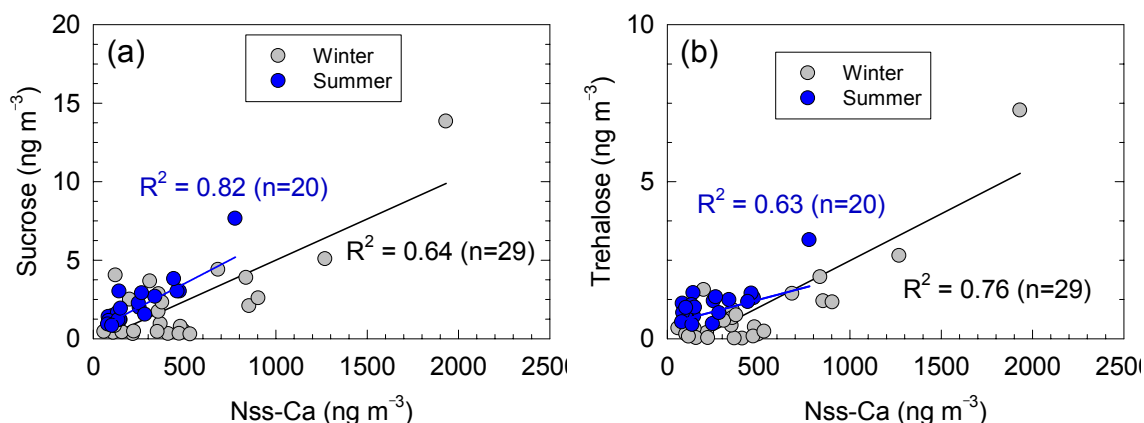


Figure 3. Relation between nss-Ca and (a) sucrose, and (b) trehalose in the Chennai aerosols.

(3) The authors state that recoveries of the quantified organic compounds were generally better than 80% (Page 21673). During the pretreatment, solvent extracts of the aerosol samples were blown to dryness with N_2 before the derivatization step. I note some relative low-molecular weight organic

compounds are among the 155 quantified compounds. Most notably are benzoic acid (MW 122) and o-, m-, p-toluic acids (MW 136). I am curious whether these small compounds were also recovered better than 80%, considering at one point the extracts were blown to dryness.

Response: We performed recovery experiments for about 80 individual organic standards following the same procedures as those for aerosol samples. When preparing for the standards, for example, the standards of benzoic acid and toluic acids, a certain amount of standards were dissolved in methanol, blown down to dryness with N₂, and then derivatized by using BSTFA at the presence of pyridine at 70 °C for 3 h. These steps are as same as those for recovery experiments, which may minimize the loss of the low-molecular weight organic compounds during the step of dryness with N₂. Actually, recoveries for several organic compounds such as malic acid, benzoic acid, pinonic acid, and pinic acid are between 60-80% (Fu et al., 2009a; 2009b). The recoveries for o-, m- and p-toluic acids (n=3) were 114 ± 10%, 80 ± 8.3% and 78 ± 7.6%, respectively. Because the solvent extraction-derivatization-GC/MS technique was well established and has been widely used to characterize the organic molecular composition of atmospheric aerosols, we just briefly stated that the recoveries for the quantified organic compounds were generally better than 80% in the text.

(4) In the conclusion section, in commenting the percent of OC mass explained by the 155 quantified compounds, the authors mentioned that part of OC mass unaccounted for is dicarboxylic acids and biogenic SOA compounds. The authors have data for dicarboxylic acids and biogenic SOA for this set of samples. Although these data are to be reported in other papers, it is relevant to give specific percent values of dicarboxylic acids and biogenic SOA compounds in this manuscript.

Response: As mentioned above, the dataset of biogenic SOA tracers will be added in the revised manuscript. Therefore, the contribution of individual compound classes to OC and WSOC will be modified accordingly. The percentage of dicarboxylic acids to OC and WSOC will also be added in the revised manuscript following the reviewer's comments. These modification and addition would make the revised paper more attractive.

References

- Fu, P. Q., Kawamura, K. and Barrie, L. A.: Photochemical and other sources of organic compounds in the Canadian high Arctic aerosol pollution during winter-spring, *Environ. Sci. Technol.*, 43, 286-292, 2009a.
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- Pavuluri, C. M., Kawamura, K. and Swaminathan, T.: Water-soluble organic carbon, dicarboxylic acids, ketoacids and α -dicarbonyls in the tropical Indian aerosols, *J. Geophys. Res.*, [Atmos], doi:10.1029/2009JD012661, 2010 (in press).
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