

Responses to Referee #1

General comments:

The purpose of the manuscript is to elucidate the chemical variability and concentration levels of 155 individual organic compounds associated with the organic fraction of PM₁₀ for the daytime and nighttime for the winter and summer seasons in Chennai (tropical India), presumably for 2008 and determine the influence of biomass/biofuel burning, plastic burning, and fossil fuel combustion. The number and compounds quantified and the selection of potential source markers and indicator compounds is outstanding. But there are substantial issues that hamper the quality of the conclusions. First, a high volume PM₁₀ sampler was employed for the sampling of semi-volatile and particle-phase organic compounds. Semi-volatile compounds may be mainly lost during sampling from the particulate matter collected and quantification of the “left-over” semi-volatiles may only indicate the tip of the iceberg so to speak. Consequently, some of the conclusions may be invalid considering that losses of semi-volatiles are typically higher in summer versus winter and seasonal comparison therefore very limited. Another major issue is the definition of summer and winter seasons and the actual days of sampling. Winter (23 January – 6 February) is only two weeks long and summer (23-31 May) only one week long. Is the short sampling duration statistical significant to warrant seasonal implications? Most likely not. Many of the numerous figures differentiate winter into “early winter” and “late winter”. With the sampling duration indicated in section 2.1 Aerosol sampling, this assumption seems to be very questionable. In conclusion, the manuscript presented highlights some episodically differences in distant source regions with major limitations due to sampling setup and sampling duration.

Response: The authors are grateful to the reviewer’s comments on this manuscript. We understand that the main concern is about the sampling artefacts and the definition of summer and winter seasons. As far as we are aware, filter sampling using a high volume sampler is a common method to collect atmospheric particles. There are mainly two types of filters. One is fiber filter (e.g., glass, quartz), the other is porous membrane filter (e.g., Teflon). We agree with the reviewer that a negative sampling artefact may occur during sampling due to a loss of semi-volatile organic compounds from the aerosols collected on quartz fiber filters by using a high volume PM₁₀ air sampler, especially during summer when the ambient temperatures are generally high. Alternatively, a positive artefact may occur during sampling due to adsorption of gaseous species on the surface of quartz fiber filters. Both evaporation and adsorption can be affected by changing pressure or temperature. In addition, oxidation of the deposited organics on the filter by oxidants (e.g., O₃, OH) may also occur during sampling.

In the present study, we collected day- and night-time samples. This time scale is reasonable to use high-volume air sampler in order to collect enough material for a detailed organic analysis using GC/MS technique. Actually, there are a large amount of documented studies that focused on the same spectrum of semi-volatile organics using high-volume air samplers to collect atmospheric aerosols at different geographical locations in the world including tropics (Simoneit et al., 1990; Simoneit et al., 1991; Kawamura and Sakaguchi, 1999; Simoneit and Elias, 2000; Alves et al., 2001; Graham et al., 2002; Wang et al., 2006; Oliveira et al., 2007).

Although the potential sampling artefacts cannot be excluded as stated above, we find several evidences that the artefacts caused by the effect of temperature on the loss of the organic species detected in the present study should be minor. **Case I:** Low molecular weight (LMW) *n*-alkanes are more volatile than high molecular weight *n*-alkanes. If we assume that the effect of temperature is significant, and the sources of *n*-alkanes remain the same during winter and summer, then the ratios of LMW *n*-alkanes to HMW *n*-alkanes should be higher in winter than in summer. However, the ratios of LMW *n*-alkanes (C₁₈-C₂₄) to HMW *n*-alkanes (C₂₅-C₄₀) detected in this study showed no significant difference between winter (0.22 ± 0.27) and summer (0.26 ± 0.23). Rather, we even found higher average ratio in summer than in winter, denying a significance of the evaporative loss. **Case II:** Phthalate esters are well-known semi-volatile organic pollutants in the atmosphere. In this study, the concentrations of phthalate esters are much higher in summer (295-857 ng m⁻³, average 553 ng m⁻³) than in winter (175-598 ng m⁻³, average 303 ng m⁻³). This again denies the importance of the evaporation artefacts. **Case III:** Three- and four-ring PAHs (LMW-PAHs) are much more volatile than those of seven- and eight-ring PAHs (HMW-PAHs). The ratios of LMW-PAHs / HMW-HPAHs in the present study were 0.16 ± 0.07 in winter versus 0.18 ± 0.05 in summer. These similar values again suggest that the effect of high ambient temperatures in summer could be negligible. Therefore, we are confident that our sampling technique is acceptable and reasonable to the subsequent discussions. These points will be added in the revision.

We defined the early winter, late winter and summer seasons in the present study due to the air mass trajectories, which are primarily controlled by the Indian monsoons (see Figure 2 in the ACPD paper). As mentioned in the ACPD paper, the trajectory plots showed three transport pathways and source regions during the campaign. In early winter (Jan. 23-28), the air masses were mainly transported long distances from North India and the Middle East. In late winter (Jan. 29-Feb. 6), the air masses were mainly transported from Southeast Asia over the Bay of Bengal. In contrast, the Arabian Sea, Indian Ocean and South Indian continent are suggested as major source regions in summer (May 22-31). Hence, we present the results of chemical analyses as three categories of season following the air mass trajectory analysis. This point will be added in the revision.

In this study, 49 samples were analyzed by GC/MS. Although the sample number is not very large, similar sampling duration scales and similar sample numbers were employed in previous studies (Simoneit et al., 2004; Wang et al., 2006; Hu et al., 2008; Yan et al., 2009). In fact, it is a really time-consuming work to characterize the organic molecular composition of atmospheric aerosols using solvent extraction, derivatization and GC/MS technique. However, less sample numbers ($n < 20$) and shorter sampling duration (several days) can be often found in previous studies (Graham et al., 2002; 2003). Thus, we don't think that our sample number is too small.

The revised manuscript will include another two compound classes (polyacids and biogenic secondary organic aerosol tracers) as suggested by reviewer #2. This is the first time that organic aerosols were characterized and reported at a molecular level in South Asia, including the compounds from both primary emissions and biogenic secondary oxidation.

References

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