Brown Carbon Absorption Linked to Organic Mass Tracers in Biomass Burning Particles

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1 Supplemental Material

1.1 Air Mass Aging

In an effort to deduce the contribution of aging to the variability in particle chemistry within the sampled air mass the relationship between specific VOCs and acetonitrile is assessed. Acetonitrile is a relatively long-lived gas-phase BB tracer ($k_{OH} = 0.02 \times 10^{-12} \text{ molec cm}^{-3}\text{s}^{-1}$) (Atkinson, 1986). Benzene ($k_{OH} = 1.2 \times 10^{-12} \text{ molec cm}^{-3}\text{s}^{-1}$) (Atkinson, 1986), propene ($26.3 \times 10^{-12} \text{ molec cm}^{-3}\text{s}^{-1}$) (Atkinson, 1986) and 1,3-Butadiene ($66.7 \times 10^{-12} \text{ molec cm}^{-3}\text{s}^{-1}$) (Atkinson, 1986) are reactive VOCs that are emitted during BB as well as various anthropogenic sources (Friedli et al., 2001). All of these VOCs are strongly correlated with acetonitrile for the two BB plumes sample (Figure S1). The two BB plumes are colored orange and brown based on the sampling periods described in the main text and in Lack et al. (2012b). If each plume were subjected to varying degrees of atmospheric processing (i.e. different photochemical ages), then one would expect to see an increasingly large difference in the VOC enhancement ratio for the more reactive VOCs (i.e. the orange and brown points would not lie on the same line). This assumes that both plumes are of the same fuel type with similar emission ratios. Figure S1, shows that the observed enhancement ratios within both BB plumes does not change indicating that mixing had a larger effect on the variability of the observed mixing ratios than photochemical processing of the BB plume. This is explained by the proximity of the fire to the measurement site and that the BB plumes were encountered prior to sunrise or very soon after.

Figure S1, Relationship of Benzene, Propene and 1,3-Butadiene with Acetonitrile.

1.2 AMS PMF Analysis

We have performed PMF analysis on the ambient organic aerosol (OA) spectra of the forest fire sampled in this study. We have explored solutions up to 10 factors, with a range of f_{peak} values (-1 to 1) (Zhang et al., 2011; Ulbrich et al., 2009). Solving for 2 factors ($f_{\text{peak}}=0$) resulted in a slightly higher Q/Q_{expected} compared to the 3-factor solution (Fig. S2a). Q/Q_{expected} did not change significantly with varying f_{peak} values; we therefore, consider $f_{\text{peak}}=0$ only. The residual between the reconstructed OA mass considering 2-factors and the observed OA mass showed a structure similar to the total OA mass during BB-II period (Fig. S3a). With the 2-factor solution, all of the signal at m/z 60 was assigned to factor 2 and the contribution of m/z 44 was most dominant in factor 1 (Fig. S2c). In the 3-factor solution ($f_{\text{peak}}=0$), the reconstruction of the OA mass was mathematically better

achieved since the structure of the residual during BB-II period disappeared (Fig. S3b). However, factors 2 and 3 were highly similar in terms of their mass spectra and time series (Fig. S2f): contribution of m/z 60 was highest in the spectra of factor 3, but non-zero in the spectra of factor 2; contribution of m/z 44 was comparable to m/z 43 in factor 3, which indicates that factor 3 had more contribution of secondary OA as well. Furthermore, both factors 2 and 3 had a hydrocarbon pattern in their spectra. Similarity in the time series of factors 2 and 3 resulted in a high correlation of both factors with furan (a gas phase marker unique to BB) as well. Solving for higher number of factors resulted in splitting of the factors; more importantly, there was no case where the signal at m/z 60 was solely assigned to one factor. Considering all these, we believe that the separation of the urban and BB emissions is not well achieved in the 3-factor solution. This is not surprising considering limitations of the PMF technique to separate factors that covary in time (which was the consequence of mixed BB and urban air masses being transported together to the site with the change in wind direction). We thus use the results of the 2-factor solution in the analysis here; however, we caution the readers to the fact that factor 2 (HOA-BBOA factor) is most likely influenced by both urban and BB emissions. In this regard, it is more straightforward to consider variability of the optical properties with the variability in the contribution of m/z 60 (f_{60}) since it is a unique marker for BBOA.

Figure S2. PMF diagnostics: (a) Variation in Q/Q_{expected} with increase in the numbers of factors solved in PMF; (b) time series of the contribution of factors in the 2-factor solution; (c) mass spectra of factors in the 2-factor solution; (d) correlation coefficient (R) between the time series and mass spectra of factors in the 2-factor solution; (e) same as b, but for the 3-factor solution; (f) same as c, but for the 3-factor solution; (g) same as d, but for the 3-factor solution.

Figure S3. Residual diagnostics of the PMF solution.