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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Biomass burning impact on PM$_{2.5}$ over the southeastern US during 2007: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis" *by* X. Zhang et al.

X. Zhang et al.

xzhang3@mail.gatech.edu

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"The analytical method utilized for the quantification of levoglucosan (HPAEC-PAD) provides high sensitivity and selectivity for various carbohydrates, which is somewhat limited by the choice of the PA1 column, as discussed in the paper. The approach taken to correct levoglucosan concentrations due to co-elution with arabitol (using a conversion factor based on mannitol concentrations) is a good first approximation, but it certainly is associated with some uncertainty. Several recent studies have shown mannitol concentrations to be variable (relative to arabitol) and even smaller in some

cases (e.g., Kundu et al., 2010). However, most previous studies have found arabitol (and mannitol) to be enriched in the coarse PM fraction. Thus, the uncertainties associated with the method used here (for fine PM) are likely not substantial, yet need to be noted, especially for measurements during warmer seasons and in wet environments (which enhances fungal activity and thus the release of these fungal tracers). The authors actually show the suitability of this method by the good agreement between measurements of levoglucosan using two independent methods (HPAEC-PAD and GC-MS). Nevertheless, an independent analytical method should also be used (in a future study) to determine an average arabitol/mannitol ratio for the specific region under investigation (and as a function of season), as both arabitol and mannitol show large spatial and seasonal differences in their ambient levels. In fact, could the poor correlation between levoglucosan and K+ during the summer months (as discussed below) be partially due to a larger uncertainty in the levoglucosan measurements during that time of year? One more comment on this issue: as the authors are probably aware of, an alternative anion exchange column (MA1) provides excellent separation of arabitol and levoglucosan."

We agree with the reviewer on the uncertainty associated with levoglucosan measurements and provide a more detailed discussion on this issue in the response to Referee #1. Although, the resulting uncertainty in levoglucosan may account for some of the poor correlation between levoglucosan and K+ in summer, we do not feel it is the main issue. Instead our results indicate that the poor correlation is from other sources of K+ becoming more important, relative to biomass-burning. This happens in summer when biomass burning K+ emissions are small (see response to Referee #1 2nd comment). The evidence for this is as follows: 1) The satellite fire count data shows much lower summertime burning and the trend between fire counts and levoglucosan concentration is consistent throughout the year (except for Jan and Dec due to indoor burning – as discussed in the paper), and there is never a correlation between K+ and fire counts (fig 8) 2) The factor analysis clearly shows a non-unique source for K+, (ie, K+ shows up as a significant component in 3 of the 4 factors, see Fig 9), and is mostly associated with a mineral dust factor (Factor 2). 3) Using leveoglucosan measured by the IC method described in this paper gives similar levels of biomass burning emissions as other source apportionment studies that do not have the same levoglucosan measurement issues. However, source apportionment based on K+ in other studies in the southeast give much higher summertime biomass burning emissions, likely because they do not consider other additional non-biomass burning sources for K+. Further issues are discussed in the following Referee #2 comments.

"The authors discuss the lacking correlation between the two biomass burning tracers (levoglucosan and K+), specifically during summer, and give a reasonable explanation for this observation, i.e., the contribution of additional sources to ambient K+, even when correcting for sea salt and soil dust. Vegetation and meat cooking have been reported as such additional sources (Lawson and Winchester, 1979, Morales et al., 1996, Schauer et al., 1999), which are both expected to be abundant in the southeastern US. However, it should also be noted that additional factors may be responsible for the large variation in LG/K+ ratios and the poor correlation between the two tracers: the relative emission factors of these species are likely also influenced by the combustion conditions, such as fire regime (flaming versus smoldering) and thus fire temperature and combustion efficiency, which can vary significantly between fires even of the same type of biomass (e.g., due to differences in moisture content). Furthermore, several studies have shown catalytic effects of alkali and alkali-earth metal ions (including K+) on the formation of levoglucosan during biomass combustion, i.e., inhibited formation of levoglucosan in the presence of K+ salts (e.g., Nowakowski et al., 2008). Thus, a number of factors (which are difficult to identify and quantify) affect the relative concentrations of the two tracers in both source emissions and ambient air."

We agree that there are a number of other factors than the ones mentioned in the paper could affect LG/K+ ratio as pointed out by the reviewer. The following statements have been added to Sect. 3.2: "The distinct seasonal trends of levoglucosan and K+, only the former tracking fire counts well, appear to be evidence that levoglucosan is a

better tracer of biomass burning (including wildfire and prescribed burning) than K+. Although poor correlation between levoglucosan and K+ can also be due to highly variable emissions, which laboratory studies show can depend on burning conditions and types of material burned (Sullivan et al., 2008), this alone cannot explain the distinctly different temporal trends of K+ and levoglucosan. The lack of correlation between fire counts and K+ clearly points to additional significant sources of K+ other than biomass burning, such as soil dust, sea salt, vegetation and meat cooking (Lawson and Winchester, 1979; Morales et al., 1996; Schauer et al., 1999), which at time can limit its use as a unique indicator of biomass burning emissions."

"The authors state that levoglucosan likely provides reasonable estimates of biomass burning contributions to PM2.5 during winter. Considering short transport distances of the smoke aerosol (as the main type of biomass burning during that time of year is residential wood combustion) and reduced photochemical activity, as well as high ambient tracer concentrations, this is a fairly safe assumption, which is also shown in the good agreement with estimates from other studies. Nevertheless, the use of ambient levoglucosan concentrations for quantitative assessments of biomass burning source contributions needs be done with caution, in particular in case the smoke particles encounter water (e.g., fog or clouds). Certainly, more research efforts are needed in this area."

Issues pertaining to loss of levoglucosan due to chemical conversion are undoubtedly another source of uncertainty when using levoglucosan as a tracer for biomass-burning emissions. This was discussed in the paper (last paragraph before conclusions).

Technical corrections

1. p. 7041, lines 15 and 17: Change "ml" to "mL"

“ml” has been changed to “mL” as suggested by the reviewer

2. p. 7043, line 19: Add "a" before "wavelength"

“a” has been added as suggested by the reviewer

3. p. 7044, line 16: Add "concentrations" after "NH4+"

“concentrations” has been added as suggested by the reviewer

4. p. 7045, line 22: Insert "the" after "limit of"

“the” has been inserted as suggested by the reviewer

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 7037, 2010.