

Interactive comment on “Flight-based chemical characterization of biomass burning aerosols within two prescribed burn smoke plumes” by K. A. Pratt et al.

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We thank J. Schneider for helpful comments and suggestions.

Reviewer: This paper presents very interesting in-situ data on the evolution of biomass burning particle in a very initial state after emission. It is well-written and the results are clearly explained (with some exceptions as detailed below). I therefore recommend publication after the following comments have been considered:

Reviewer: Major Comments: I have one major concern regarding the O/C ratios inferred from the C-ToF-AMS. The relationship between f44 (m/z 44 / total organics) and O/C from Aitken et al., 2008, (Equ. 1 in the present paper) was derived from HR-ToF-

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AMS data. My own experience from running a C-ToF parallel to a HR-ToF shows that the f44 values measured by a C-ToF are higher than those measured by the HR-ToF, and thereby the calculated O/C ratios may be too high. This may be due to higher fragmentation or due to lower ion transmission of larger m/z . The magnitude of this effect appears to be dependent on the actual tuning of the ion extractor and/or the mass spectrometer voltages. So, unless there is no experimental verification for the relationship between f44 and O:C from C-ToF data, I suggest to remove the statements on O:C ratios and report only the f44 values. Once the relation between f44 and O:C for the C-ToF has been established by laboratory measurements, the O:C values can easily be calculated later on.

Authors: To our knowledge, there have been no publications indicating that the (m/z 44 / total organics) ratio is different for the C-ToF-AMS vs. HR-ToF-AMS instruments. Since both instruments use the same vaporization and ionization techniques, we do not know of a physical reason to expect them to be different; therefore, we have decided to leave the estimated O/C ratios in the paper.

Reviewer: Additionally, the effect of elevated gas-phase CO₂ (as mentioned at the end of section 2.3) may disturb the inferred O/C ratios. Can the delta CO₂ (not measured) be estimated from delta CO?

Authors: We did not attempt to correct CO₂ based on CO because CO data were not available for period 1 and when available the large range of CO:CO₂ emission factors observed would make this estimate unreliable.

Reviewer: Minor Comments: Section 3.2: Page 17520, lines 4ff and Figure 4: In our recent observations (Brands et al., AS&T, 2011), we detected Na⁺ along with K⁺ in biomass burning mass spectra, using the same ablation laser (266 nm). It amazes me that the data presented here don't show any Na⁺ signal.

Authors: Silva et al. (1999) examined the ATOFMS mass spectra resulting from the combustion of a variety of biomass fuels, and it was observed that the Na⁺ signal varied

significantly when burning different fuels. Also, McMeeking et al. (2009) showed that the emission factors associated with Na^+ are generally significantly lower than those for K^+ ; however, these vary significantly between fuels with sagebrush having a high potassium emission factor compared to sodium.

Reviewer: Page 17521, Line 25 ff: EC/BC particles smaller than 100 nm may not be detected by ATOFMS. Maybe there is a fraction of non-coated, small soot particles that are missed.

Authors: This is a good point. It is now noted that “no EC particles larger than 70 nm (dva) were observed.”

Reviewer: Section 3.3.1: Page 17532, line 9: While I fully agree that aging and mixing increases the O:C ratio, I am skeptical about the absolute values, as already stated above. The reason that your O/C after 80 min is higher than Grieshop O/C after 5 h may be the above mentioned C-ToF-AMS effect. Grieshop used a Quad-AMS, I am not sure if f44 from Quad data are comparable to C-ToF data.

Authors: As discussed above, a systematic difference in f44 between AMS instruments with different mass analyzers is not expected and has not been published. However, given more recent work in the study of the aging of biomass burning organic aerosol, the Grieshop reference has been replaced by more relevant recent studies (Hawkins and Russell, 2010; Hennigan et al., 2011; Kessler et al., 2010).

Reviewer: 17524, line10: “=” misses

Authors: This typo has been fixed.

Reviewer: 17525, line 15ff: Is m/z -71 only due to levoglucosan in the A-ATOFMS spectra? Or may there be other contributions from organic acids?

Authors: m/z -71 ($\text{C}_3\text{H}_3\text{O}_2^-$) is a significant ion peak in the negative ion mass spectrum of levoglucosan (Silva et al., 1999). The presence of levoglucosan is consistent with the elevated (m/z 60/total organics) ratio measured by the C-ToF-AMS. However, re-

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cent studies in our laboratory (unpublished) do suggest that certain organic acids can contribute to m/z -71; therefore, this paragraph about levoglucosan has been reworded and reorganized.

Reviewer: 17526, line 7: the sentence after “similarly: : :” refers to A-ATOFMS data, correct?

Authors: Yes. This sentence has been clarified to say “Similarly, the A-ATOFMS number fraction. . .”.

Reviewer: Sections 3.3.1 and 3.3.2 both end with: ”: : :the behavior of : : : during the initial aging of biomass burning particles/aerosol is unclear : : : and requires further study.”

Authors: These sentences have been removed since they were unnecessary.

Reviewer: Section 3.3.3 and Conclusions: Acidic particles? Is this result based on A-ATOFMS or on AMS data? From section 3.3.3 this was not clear to me. Maybe a plot of NH_4 vs. $\text{SO}_4 + \text{NO}_3$ (from AMS) would help to see whether sufficient NH_4 was present to neutralize the acids.

Authors: Particle acidity was evaluated primarily through examination of the A-ATOFMS data. This discussion was reorganized as follows: “During RF03 Period 1, the calculated C-ToF-AMS $\text{NH}_4 + \text{meas}/\text{NH}_4 + \text{neu}$ ratio (Zhang et al., 2007) was calculated to be 0.40 ± 0.08 , indicating the presence of acidic particles. The A-ATOFMS number fraction of acidic particles increased with aging, as evidenced by the trend of the sulfuric acid ion marker m/z 195($\text{H}_2\text{SO}_4\text{HSO}_4^-$) (Denkenberger et al., 2007; Yao et al., 2011). The number fraction of biomass burning particles internally mixed with sulfuric acid increased from $8 \pm 4\%$ at ~ 2 -4 minutes of aging to $28 \pm 4\%$ at ~ 32 -39 minutes and then stayed relatively constant with aging to ~ 81 -88 minutes. For a plume age of ~ 17 -30 minutes, $12 \pm 3\%$ of RF01 biomass burning particles were mixed with sulfuric acid.” Unfortunately, the AMS statistics were not sufficient to examine particle acidity

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during the other plume periods.

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