**Atmospheric
Chemistry
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Discussions**

Interactive
Comment

Interactive comment on "Boreal forest fire emissions in fresh Canadian smoke plumes: C_1–C_{10} volatile organic compounds (VOCs), CO_2, CO, NO_2, NO, HCN and CH_3CN" *by* I. J. Simpson et al.

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1. This paper is about measurements and interpretation of VOCs, CO2, CO, NO2, NO, HCN, and CH3CN from fresh Boreal forest fires. This is good contribution to the growing body of knowledge for fire emissions. The paper is well written, well organized, and concise. CO2, methane, and CO were found, not surprisingly, to comprise nearly all of the carbon released from the fires. The speciated VOC measurements were comprehensive and showed that indeed a wide range of VOCs are emitted from these fires and that the amount of total carbon released in this form, although less than 2 % of the

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total carbon released, is notable as it has implications for global budgets for individual species. It was interesting that these were the first reported monoterpene emissions form Boreal forest fires. Although it is not surprising that there are emissions of these species from fires, as the authors correctly explain because of the stored terpene pools known to be present in the conifers of these forests, this is a new finding that can be used to improve models, with special implications for particle formation. The terpenes and C1-C2 species comprised the bulk of the VOC emissions from these fires. The strong contributions of the light VOCs have been established in the literature and this study supports that. The measurements of species found not to be emitted by fires is informative. The information obtained on the chlorocarbons is timely and helps with our understanding of the attribution of sources of these species and for specific compounds like dichloromethane provides hard data which points to little or no emission from Boreal fires in this region of the world. The whole air sampling technique was employed in this study and the resulting air samples were analyzed by well established analytical techniques. Other key species were included in the analysis as noted above.

- We thank Reviewer 1 for these comments.

2. I believe the discussion on acetone p. 9531-95-32 should be left out because work by Hornbrook et al., (Observations of volatile organic compounds during ARCTAS – Part 1: Biomass burning emissions and plume enhancements, Atmos. Chem. Phys. Discuss., 11, 14127-14182, doi:10.5194/acpd-11-14127-2011, 2011), also taken from the ARCTAS DC-8 measurements but using other data that were available on the plane and looking at in more detail, show that there is little or no discrepancy for the acetone ERs (or more specifically enhancement ratios) with literature values.

- We have thought carefully about the question of acetone, both in response to this comment and in the original paper submission. Our group reports an acetone-to-CO emission ratio (ER) of 1.6 ± 0.4 pptv/ppbv for fresh biomass burning plumes (P9532); Hornbrook et al. (2011) report a mean normalized excess mixing ratio (NEMR) of 5.9 ± 4.0 pptv/ppbv for Canadian biomass burning; and Singh et al. (2010) report an en-

hancement ratio of 4.7 $\pm$ 3.3 pptv/ppbv for ARCTAS. Note that these values are not statistically different from one another and they are also not the same thing. The ER is an estimate of the starting emission ratio, while the average NEMR is the average value observed in a random selection of plumes of many ages. Jost et al. (2003) have previously observed an increase in the acetone-to-CO ratio during plume aging (P9532, L16-17). As cited in Hornbrook et al., acetone-to-CO values from biomass burning in various ecosystems range from 1.5-2.1 pptv/ppbv for young fire plumes (Friedli et al., 2001; Holzinger et al., 2005) to 19.5-30 for aged fire plumes (Singh et al., 1994; Andreae and Merlet, 2001). That is, our ER for fresh smoke plumes sampled during ARCTAS lies within the range for young fire plumes in other ecosystems. On the other hand, it is important to recognize the inherent variability of fire plumes (both within a single plume and between plumes) and the resulting lack of clarity in comparing the average NEMR from a random selection of "young" and "aged" plumes to our ER, because the variability may mask an underlying aging trend in some cases; e.g., see Lefer et al. (1994) and Hornbrook et al. (2011). In our case, because the ERs/enhancement ratios for the various ARCTAS research groups are not significantly different from one another, and because our values lie within the range reported in the broader literature, especially for young plumes, we do not see a clear reason to justify omitting the discussion. Our group was very cautious with the plume selection and it is still our belief that the statistically significant difference between our results and those of de Gouw et al. (2006) is most likely due to fire-to-fire variability, although we cannot rule out a component due to aging effects.

To address the reviewer's comment, we have changed the text as follows:

"Two compounds that disagree with some literature values are acetone and ethene. The acetone ER reported here (1.6 $\pm$ 0.4 pptv ppbv-1) is statistically lower than the Enh.R. reported by de Gouw et al. (2006) (6.3 $\pm$ 1.8 pptv ppbv-1), which is an average ratio from 11 aged forest fire plumes from Alaska and western Canada sampled in July, 2004. This difference lies well outside our measurement uncertainty of 30%,

which includes potential wall losses inside the canisters (Section 2.2). The UC-Irvine ER is also lower than other values reported for ARCTAS (Singh et al., 2010; Hornbrook et al., 2011), though the differences were not statistically significant. Singh et al. (2010) reported a mean Enh.R. of 4.7 ± 3.3 pptv using high-frequency in situ PTR-MS measurements in fresh biomass burning plumes (0-2 km), nearly all of which were sampled during ARCTAS-B (H. Singh, pers. comm., 2011). Hornbrook et al. (2011) reported 5.9 ± 4.0 pptv ppbv−1 for Canadian biomass burning of all ages sampled during ARCTAS-B using the Total Organic Gas Analyzer (TOGA), with individual plume values ranging from 1.7 ± 0.7 to 16 ± 1 pptv ppbv−1. Whereas Jost et al. (2003) have previously observed an increase in the acetone-to-CO ratio during plume aging by means of secondary acetone formation, the natural variability of fire plumes can obscure the aging trends in many cases, as observed by Lefer et al. (1994) and Hornbrook et al. (2011). Based on our previous experience with oxygenated species we suspect that the statistically significant difference between our results and those of de Gouw et al. (2006) is primarily related to fire-to-fire variability, but we cannot rule out a component due to aging affects. The difference in ethene ERs between this study and Goode et al. (2000) is expected to be related to emission variability since both studies used only fresh smoke."

3. P9524 line 24: lifetime is given but under what assumptions?

- We're assuming the reviewer is referring to P9534 line 24. In this case, the 47 day lifetime for ethane is under the conditions stated in Table 1, namely a 12-hour daytime average OH concentration of 2×10^6 molec cm-3 and an OH rate constant from Atkinson and Arey (2003). As noted in the Table 1 footnotes, the ethane lifetime may be even shorter in the smoke plumes due to elevated OH levels. To clarify the lifetime assumptions, we now refer the reader to Table 1 in the discussion on P9534 line 24.

4. P9528 line 28: : : :.they are difficult to speciate using these techniques due to spectral overlap ... this is strictly true for IR techniques – for the MS technique it is more correct to state that it is difficult to speciate because the mass spectrum resulting

from ionizing the various terpenes results in an identical, indistinguishable, isobaric product ion.

- We agree with the reviewer's correction. In our case we used gas chromatography coupled with MS detection to achieve a good separation of the two pinenes using a DB-5ms column. We have clarified the text on P9527 line 27 as follows: "Monoterpenes have been observed in smoke by mass spectrometric or infrared spectroscopy techniques, but they are difficult to speciate using those techniques due to spectral overlap of the various monoterpene features for IR techniques, and due to an indistinguishable product ion for MS techniques (Yokelson et al., 1996). By contrast, here we achieved a good separation and accurate speciation of the pinenes using MS detection coupled with gas chromatography using a DB-5ms column (Simpson et al., 2010)."

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 9515, 2011.