Atmos. Chem. Phys. Discuss., 11, C8981–C8987, 2011
www.atmos-chem-phys-discuss.net/11/C8981/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evolution of trace gases and particles emitted by a chaparral fire in California" *by* S. K. Akagi et al.

Anonymous Referee #1

Received and published: 15 September 2011

Review of "Evolution of trace gases and particles emitted by a chaparral fire in California" by S.K. Akagi, et al. submitted for publication in Atmospheric Chemistry and Physics.

The authors present the results of new in-situ field measurements of several ambient gases and particle properties inside a smoke plume from a prescribed fire of chaparral fuels in California in November 2009. Measurements made directly at the fire source were used to characterize the primary emissions and determine the emission ratios (ERs) and calculate emission factors (EFs) of 18 gas-phase species as well as particle composition and optical properties. The uniquely isolated fire plume was then systematically measured at discrete distances downwind of the source in order to study the gas-phase photochemistry and particle transformations within the "ag-

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ing" fire plume. The collective measurements clearly indicate that OH oxidation within the plume resulted in a decrease in the primary reactants (e.g., C2H4 and NOx) and the subsequent photochemical formation of secondary products (e.g., O3, HCOOH, CH3COOH and PAN) on the timescale of 0-4.5 hours after initial emission at the fire source. Notable results of the particle measurements include the overall decrease in OA with plume aging while particle scattering (bscat) increased. The authors compare the chemical evolution of the Williams Fire to that of a previously documented tropical biomass burning plume(s) in Mexico in March 2006.

The measurement techniques and scientific methods included in this analysis are robust and the data collected represents a unique and valuable dataset. The findings of this analysis are of significance to a wide audience, particularly to those interested in the composition, chemistry and climate impacts of biomass burning. The topic is certainly relevant to readers of ACP. I recommend publication after revision.

General Comments:

1. It would be incredibly useful if all of the findings discussed in sections 3.2.1 to 3.4 were summarized in a new table(s). This table should include the fire-average initial molar emission ratios and standard deviations included in Figures 5-12 and the final measured or fitted NEMRs at age = 4-4.5 hours for all the relevant species/parameters. Additional columns could include the net and relative changes of the Williams Fire. Since the Yokelson (2009) analysis of the Mexican plume is repeatedly compared to the Williams Fire, I suggest adding a column to the new table that has the relative change of the Yucatan plume at t = $\sim$1.5 hour for ease of comparison. This would also simplify and reduce the amount of repetitious text throughout Sect. 3.2 to 3.4.

2. The data presented in Table 2 isn't directly applicable to the subsequent discussion. The slope-based source ERs and uncertainty in Table 2 are not used in the discussion of the plume evolution, the mean and standard deviations are. Furthermore, Burling (2011) has already published MCE and EFs for the Williams Fire given in Table 2.

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Since there is little to no discussion of the MCE and EFs in the text, there is little need for them to be included here. I suggest removing Table 2, especially if the new table mentioned above is included.

3. The purpose of Sect 3.1, other than an introduction to Table 2, is unclear. The authors discuss the difference in the uncertainties in ERs using the slope-based approach versus the standard deviation of the mean; however, it isn't entirely clear why one uncertainty is a better metric than the other based on the amount of plume mixing. I understand that it is difficult to estimate mixing, but what (if anything) can be learned from the long-lived species with relatively large emissions in the fire such as CH4 and C2H2? Wouldn't a decrease in these long-lived species inside the plume point to mixing of the fire plume with background air (i.e., dilution) since chemical destruction/production on the <4 hour timescale be negligible?

4. I would suggest using the more specific "elapsed time" or "time since emission" rather than the general term "age," which has a similar connotation as photochemical age and atmospheric lifetime, etc.

5. It can get confusing for the reader when the absolute ERs and NEMRs and the relative changes with aging are discussed in the text in percents, fractions and factors. For example, on P22503 the discussion of the change in organic acid ratios are given in Fig. 6 and Table 2 as a straight fraction but referred to in the text as a percent. The net changes in the organic acids are given as factors while the net ΔHCHO/ΔCO is given as a percent. I suggest limiting the use of percents except where necessary.

6. The role of HONO is not discussed in this manuscript even though it had an appreciable EF. HONO would be an additional source of OH in the daytime fire plume. The authors state that the difference in estimated OH between the Williams Fire and the African+Mexican fires is due primarily to the amount of solar radiation, but how comparable were the sources of HONO?

7. Not much is mentioned regarding the relative timescales of the quick production

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of particulate ammonium and the slow/indistinct loss of ammonia as the plume ages, as shown in Figure 8. Could the large uncertainty in the gaseous NH3 at the source be a product of variable emissions compounded by quick conversion to particulate ammonium?

8. It is clear that $\Delta OA/\Delta CO2$ decreased from 0.00355 to 0.00266 over the 4 hours since emission. However, I don't think that much can really be said about the initial decrease in the $\Delta OA/\Delta CO2$ ratio followed by a slow increase as shown in Figure 11. How was this fit/trend determined? It looks as if a simple exponential curve would also fit the same data points just as well.

Specific and Technical Comments:

P22486 L13: Does the summary of BB in the "continental US" include Alaskan fires? If not, I would use the term "contiguous US."

P22495 L1: The term "nascent" should be clearly defined. I believe that the authors use this term to identify the freshest samples (0-10 min from emission) where it has been determined that little to no aging has occurred.

P22495 L9: The description of how the smoke age and estimated emission time were determined should be moved to the first paragraph of Sect 2.3 when describing the contents of Table 1.

P22496 L27: Change "different time response of instruments" to "different time responses of the instruments."

P22498 L19: OC is not defined in the text.

P22500 L1-2: ". . .plume aging results were not obtained. . ." This wording is confusing.

P22500 L5-11: The brief comparison of the PM2.5 EF given in Sect 3.1 could be moved to Sect. 3.3 especially if Table 2 is removed.

P22500 L11: "Rather than emphasize late samples of smoldering combustion. . ." I am

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not sure what the authors are trying to say here. Does “emphasize” mean “measure” or is it referring to the relative weighting of certain data points? What does “late” refer to? If this sentence describes the sampling strategy, then it should be moved to Sect. 2.3.

P22500: Section 3.2 should be renamed “Plume evolution” in keeping with the title of the manuscript.

P22500 L25-P22501 L4: The description of how the “smoke age” and “estimated emission time” were determined should be moved to the first paragraph of Sect 2.3 when describing the methods used and the contents of Table 1.

P22501 L4-7: It would make more sense if the discussion of NH3 was moved to Sect 3.2.4. Additionally, I don’t follow the logic stated here. If you have greater uncertainty in the source emission ratio (presumably due to changes in emissions at the source), then one would expect that this would carry through to the downwind measurements (uncertainty = changes in source emissions + chemical and physical aging). For those species whose source emission ratios did not vary as much, then the differences downwind would reflect the changes due to chemical and physical aging (only).

P22501 L7-20: The authors discuss the nuances of Figures 6-12, which aren’t discussed until P22503, and before Figure 5 is referred to. In order to avoid unnecessary confusion and have the discussion follow a more logical progression, I suggest the following:

(a)Simply switch the placement of Sect 3.2.3 and Figure 7 regarding ozone with Sect 3.2.1 and Figure 5 regarding the alkenes and estimation of OH

(b)The discussion and introduction of the aging plots and fits (currently L7-20) could now be included in Sect. 3.2.1 using the ozone plot as a direct reference in sequential order.

P22501 L21-L26: This paragraph includes an important discussion on the source ERs

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as a function of altitude and should be moved to Sect 3.1 (or later) when source ERs are first discussed.

P22505 L2: There is enough scatter in both the source ER as well as the downwind NEMRs that the trend for NH3 is anything but "clear." Perhaps the ΔNH3/ΔCO aging plot mentioned shows a more distinct decay?

P22508 L12: Figure 9b does not show ΔPAN/ΔNOx.

P22509 L21: It should be clearly noted that Cl atom has an appreciable rate coefficient with C2H2 so that the presence of Cl atoms in the plume would result in a decrease in ΔC2H2/ΔCO. The fact that the ratio didn't change may also give some indication that there was minimal mixing of the plume with background air.

P22514 L2: It is more accurate to simply state that $\sim$ 50% of the initially emitted rBC particles are "thickly coated" as shown in Figure 12. The remaining 50% is classified as either "thinly coated" or "not coated" at the time of emission.

P22516 L16: It is sufficient to say that the plume was photochemically active.

P22533: Remove comma between "a.m.s.l, (purple)"

P22537 Figure 5 caption: k1 and k2 are not defined in the text. These should be changed to kethylene and kCO to match the discussion in text.

P22538 Figure 6 caption: The text "with plume aging (h)" should be changed to "estimated smoke age (hr)" to be consistent with the figure and subsequent figure captions. It should be clearly stated that the blue markers and error bars are the mean and standard deviation of the 10 source samples. The error bars on the black and red points at t=4.5 should be defined here.

P22539 Figure 7 caption: Is the y-intercept from Table 2 (slope-derived ER) or is it the mean?

P22540 Figure 8 caption: The error bars for data at t=4h is not defined.

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P22541: The blue points representing the source averages should be on top of the individual measurements so that you can see the mean $\pm$ s.d. Again, the error bars for the black and green data points are not defined in the caption. The abbreviated unit for hours should be consistent throughout the text, figure captions and axis labels. The figures have (hr) and some of the text refers to (h).

P22542 Figure 10c: The blue data point should be on top.

P22543 Figure 11: There are no blue data points showing the source mean ER for either parameter.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 22483, 2011.