Atmos. Chem. Phys. Discuss., 12, C11664–C11677, 2013
www.atmos-chem-phys-discuss.net/12/C11664/2013/

Atmospheric
Chemistry
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Discussions

Interactive comment on "Measurements of reactive trace gases and variable O_3 formation rates in some South Carolina biomass burning plumes" *by* S. K. Akagi et al.

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Received and published: 16 January 2013

We thank both Referees for excellent comments that will strengthen the paper. Our response to each comment is described below.

Anonymous Referee #1 This well-written paper presents data and analysis from prescribed forest fires in the southeastern United States. Measurements were taken by FT-IR and whole air sampling (WAS) at ground level and from aircraft, providing an opportunity to contrast lofted and low-lying emissions from the same fire. Emission factors (EFs) are provided for a large number of compounds and are compared to data from a previous study of ecologically similar fires. The significant differences in EFs between these two studies illustrate the under-constrained and highly variable nature of biomass burning emissions. The authors focused their analysis on a few topics, including the presence of monoterpenes in the initial emissions as well as their role in the chemical evolution of the plume. They also discuss the chemical evolution of other species in the plume including ozone and methanol. HCN is highlighted as reliable biomass burning tracer, particularly for lofted emissions.

I recommend publication and ask the authors to consider the following questions and comments to improve their very good manuscript.

R1.1. You discuss the rapid dilution of the observed plumes as a limiting factor in your ability to study the aging of the plume, but you do not state the cause of the fast dilution. Were these spatially small plumes, or were they subjected to unusually rapid mixing? Did high background mixing ratios have a large role in losing track of the plume?

A1.1. There are a number of relevant factors governing downwind excess values in plumes and the referee has indeed identified the main ones. Given the high amount of prescribed burning near populated areas in the SE US, land managers restrict prescribed fires to days with good atmospheric dispersion, which is in turn promoted by (1) atmospheric instability, (2) high vertical mixing heights, and (3) robust transport winds. Mostly cloud-free skies during our mission promoted strong solar insolation and surface heating, good afternoon vertical mixing, an unstable atmosphere, and deep mixed layers (1100-1600 m). The transport winds were moderate at 4-10 m/s. Thus the elements required for good dispersion were in place. In addition, the numerous other pollution sources in the region led to a fairly polluted boundary layer (BL), which meant plume concentrations had to be reasonably high to be distinguished from background. The Williams Fire in California was of a similar size to those in SC, but the boundary layer was significantly thinner (450 m AGL) and the downwind plume that was sampled diluted above the boundary layer in the free troposphere where vertical mixing is much slower than in the BL. In fact the downwind tip of the plume was only several hundred meters thick. For the Timbavati Fire smoke dispersion occurred under meteorological conditions that were actually very similar to those in SC, but the Timbavati Fire burned about 20-30 more area (1000 ha) in about the same amount of time as the SC fires and the higher downwind excess CO values were probably due to a stronger source strength.

To clarify these points we have made the following changes.

P25268, L14-16 -Original text: “The plumes diluted rapidly mostly in the top half of a somewhat hazy boundary layer due to variable winds (mixed layer extended to ∼1100m above mean sea level, a.m.s.l.).” -Revised text: “The plumes diluted rapidly mostly in the top half of the already-polluted boundary layer due to brisk, shifting transport winds (4-10 m s-1) and strong vertical mixing (unstable atmosphere with the mixed layer extending to ∼1100-1600 m above mean sea level, a.m.s.l.).”

P252269, L10-12 -Original text: “The plumes from these three fires also diluted rapidly in the boundary layer to form broad “cone-shaped” plumes under the influence of light and variable winds.” -Revised (more accurate) text: “The plumes from these three fires diluted rapidly, like the Fort Jackson plumes for similar reasons, and formed broad “cone-shaped” plumes in the boundary layer.”

P25283, L7 -Original text: “Plume aging data were collected from the aircraft on four fires: Block 9b (1 November), Georgetown (7 November), Francis Marion (8 November), and Bamberg (10 November). However, the “useable” data from this study were strongly limited by the extremely fast dilution rate of the plumes. For context,. . .” -Revised text: “Plume aging data were collected from the aircraft on four fires: Block 9b (1 November), Georgetown (7 November), Francis Marion (8 November), and Bamberg (10 November). However, the “useable” data from this study were strongly limited by the low excess mixing ratios in the downwind plumes. For context,. . .”

P25283, L19-23: -Original text: “In fact, DCO from the Bamberg fire was often less than 50 ppb in the source smoke and only one source sample had DCO > 250 ppb, which shows the effect of rapid dilution even at the source. A consequence of this rapid dilution is a downwind SNR often 30–40 times lower in SC than at the Williams Fire or Timbavati Fire." -Revised text: "The higher downwind DCO values on the Williams Fire occurred mainly because the plume diluted above the mixed layer with minimal vertical mixing. The downwind smoke on the Timbavati Fire was likely more concentrated because that fire burned 20-30 times more area than the SC fires in about the same time, contributing to a stronger source strength. A consequence of the low downwind DCO values in SC is a SNR in the downwind samples that was often 30–40 times lower in SC than at the Williams Fire or Timbavati Fire."

R1.2. The observed ozone production is discussed in the context of a diverse set of other studies. Aside from attributing the high production rate of the Block 9b plume to mixing with anthropogenic emissions and the lower rate of the Bamberg fire to cloud cover, no explanations are offered as to what made these fires rapidly produce ozone. If you can provide insight here, it would be helpful. Also, why is ozone formation ubiquitous in tropical biomass burning plumes but not in extratropical plumes? A citation or a sentence of explanation would be beneficial.

A1.2. The fastest O3 production occurred on a sunny day when there was mixing with urban NOx, and the slowest occurred when there was high cloud cover and little or no NOx input from urban areas. Intermediate rates of O3 formation occurred with clear skies, but little or no NOx input from urban areas. We agree that we have not attempted to explain why the intermediate rates of ozone production during this extra-tropical study happened to be similar to rates measured in tropical plumes or why the rates were faster than in the Williams Fire in all cases. It could be ubiquitous, small-scale NOx sources, or biogenics, or other factors, but a modeling study would probably be required to clarify this. The idea that O3 formation is ubiquitous in tropical plumes, but not in extratropical plumes is not surprising given the higher reactivity of the tropical atmosphere on average, but we feel it is beyond the scope of this paper to prove this. Instead the statement is just our impression based on studying the available literature as exemplified by Andreae et al., (1994) or summarized in Akagi et al. (2011) and Jaffe and Wigder (2012). These references are now added.

P25286, L22: after "plumes" we have added "(Andreae et al. 1994; Akagi et al. 2011; Jaffe and Wigder, 2012)"

In references we have added: "Jaffe, D. A., and Wigder, N. L.: Ozone production from wildfires: A critical review, Atmos. Environ., 51, 1-10, 2012."

R1.3. Is loss of analyte in the WAS canisters a concern? I am specifically wondering about samples that initially contain ozone and monoterpenes.

A1.3. This is a concern that we both took steps to prevent and investigated post-experiment, which should be made clearer in the text. In general, all the canisters were filled between 30 Oct and 2 Nov and then analyzed on 4 Nov, so (dark) storage times were less than the 7-day recommended limit based on storage tests conducted at UC-Irvine in the past (Simpson et al., 2011). In addition, all the WAS samples were collected in fresh smoke with depleted O3, except for one downwind canister collected on 1 November that did not factor into the calculation of reported quantities. Also, as already mentioned (P25269, L23), ER to CO based on the canister samples were typically within 20% of the ER to CO based on the FTIR samples for overlap species – even for limonene. To provide a more accurate depiction of the dark storage times we changed the text as follows.

P25263, L28: -Original text: "All 24 canisters were sent to UC-Irvine for immediate analysis of 89 gases: CO2, CH4, CO, carbonyl sulfide (OCS), dimethyl sulfide (DMS), and 83 NMOCs by gas chromatography (GC) coupled with flame ionization detection (FID), electron capture detection (ECD), and quadrupole mass spectrometer detection (MSD)." -Revised text: "All but one WAS sample was collected in fresh smoke with depleted O3 (see Sect. 3.7) and all WAS samples were analyzed for 89 gases within 2-5 days of collection (to minimize potential loss or growth of certain analytes within the canisters; see Simpson et al., 2011). CO2, CH4, CO, carbonyl sulfide (OCS), dimethyl sulfide (DMS), and 83 NMOCs were quantified using gas chromatography

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(GC) coupled with flame ionization detection (FID), electron capture detection (ECD), and quadrupole mass spectrometer detection (MSD)."

R1.4. Have you compared the Picarro data with the AFTIR data for CO2, CO and CH4?

A1.4. The very different response times and sampling strategy of the AFTIR and Picarro make a meaningful intercomparison difficult. However, both the Picarro and the AFTIR were calibrated with the same NIST-traceable standards. The fact that the Picarro shared an inlet with the aerosol instruments and that the Picarro inlet was co-located with the AFTIR inlet, which was calibrated with the same standards as the Picarro was planned in advance to optimize overlap between the trace gas and aerosol measurements. We now clarify this:

P25264, L24-27: -Original text: "A Picarro cavity ring-down spectrometer measured H2O, CO2, CO, and CH4 at 0.5Hz during flight. Ratioing the particle data to the Picarro CO measurements allowed synthesis of the particle data with the AFTIR and WAS trace gas measurements on the aircraft..." -Revised text: "A Picarro cavity ring-down spectrometer measured H2O, CO2, CO, and CH4 at 0.5 Hz during flight, and used the same sampling inlet as the particle instruments. The particle/Picarro inlet was located adjacent to the AFTIR inlet and the Picarro was calibrated inflight with the same standards used to characterize the AFTIR retrievals. Thus, ratioing the particle data to the Picarro CO measurements allowed accurate synthesis of the particle data with the AFTIR and WAS trace gas measurements on the aircraft..."

P25264, L21-24: The following sentence was moved to the end of Section 2.4 so the flow is more logical: "Measurements of the aircraft position, ambient three-dimensional wind velocity, temperature, relative humidity, and barometric pressure at 1-Hz were obtained with a wing-mounted Aircraft Integrated Meteorological Measuring System probe (AIMMS-20, Aventech Research, Inc.) (Beswick et al., 2008)."

R1.5. Page 25276, line 28: this sentence is confusing with so many qualifiers. Improving the clarity would be beneficial.

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A1.5. We have made the following changes: -Original text: “Most commonly in wildfires, especially boreal forest fires, it is sometimes the case that much of the fuel is consumed at night by smoldering or even flaming combustion that is perhaps promoted by nighttime frontal passage (Vermote et al., 2009; Turetsky et al., 2011).” -Revised text: “In a small minority of prescribed fires and more commonly in wildfires (especially in the boreal forest), a large amount of fuel can be consumed at night by smoldering combustion (Turetsky et al., 2011). On occasion, flaming combustion can occur at night that is perhaps promoted by nighttime frontal passage (Vermote et al., 2009).”

R1.6. Page 25277, line 8: giving one value (90 or 91) would probably suffice given the preceding “about.”

A1.6. Done, “about 90–91%” is now “about 90%”

R1.7. Page 25277, line 13: you state that nighttime fires probably have higher monoterpene emissions and that most of the monoterpenes will be oxidized by NO3, but you don’t say why the monoterpene emissions would be higher. Are the higher nighttime emissions inferred from the higher ground-based ERs compared to the airborne ERs, recognizing the lower MCE of nighttime fires?

A1.7. Yes, the Referee makes a good point. At night, the relative humidity, fine-fuel moisture, and atmospheric stability tend to increase while temperature and surface winds tend to decrease. All these factors could increase the smoldering to flaming ratio (lower the MCE) and therefore also increase the monoterpene emission factor. The tendency for more smoldering at night was added to the paper as follows:

P25277, L13-14 -Original text: “However, some fires produce smoke at night that probably has higher monoterpene content and most of those monoterpenes would be oxidized by NO3.” -Revised text: “However, some fires produce smoke at night. Nighttime combustion is usually dominated by smoldering combustion due to higher relative humidity, lower temperature, lighter surface winds, and other factors. Thus, nighttime smoke probably has low average MCE and high monoterpene content. Most of the

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monoterpenes emitted during the night would be oxidized by NO3."

R1.8. Page 25280, lines 21-23: isn't MCE=0.96 by definition not smoldering combustion?

A1.8. This sentence was unclear and we have changed it as follows. -Original text: "Overall, the airborne and ground-based EF(HCN) show a strong negative correlation with MCE suggesting that HCN is released from smoldering combustion over a wide range of MCEs (0.85–0.96) (Fig. 11)." -Revised text: "Overall, the airborne and ground-based EF(HCN) show a strong negative correlation with MCE over a wide MCE range (0.85-0.96), suggesting that HCN was primarily released from smoldering combustion (Fig. 11)."

R1.9. Page 25304: in the "Atmospheric conditions" column, you use inches and feet. It would be better to use SI units.

A1.9. Change to mm and m made – thank you.

R1.10. In Figures 2-4, the symbols used for fire locations, hotspots, and sample locations are very similar, especially the fire locations and hotspots. Using a different symbol for fire locations would improve the maps.

A1.10. We have now used large solid circles for the fire locations and squares for the sample locations.

R1.11. The colors used in Figure 13 for SC and CA data are fairly similar– changing one of the colors or using different symbols would improve clarity.

A1.11. We have changed the CA data to green circles.

Anonymous Referee #2

The manuscript presented emission factors for 97 trace gas species measured from prescribed fires in South Carolina, US using Fourier transform infrared spectrometer (FTIR) and whole air sampling (WAS) in October-November 2011. It provides a most

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comprehensive suite of measurements of trace gas species emitted from temperate forest fires. The results were compared with previous measurements of fire emissions, and demonstrated the variability and uncertainties in trace gas emissions from prescribed fires. The study further examined ozone photochemical production rates in four measured fire plumes downwind, and showed large ozone production on a sunny day when fire emissions mixed with urban emissions. The study also showed evidence of post-emission methanol and formaldehyde production in fire plumes. The manuscript is comprehensively summarized and well written. It will provide an improved picture of prescribed fire emissions in the southeast US and their impacts on air quality. I recommend publish on ACP after the following minor comments been addressed.

Comments:

R2.1. Page 25270, Line 2-5: Can you please comment in Figure 5 why the emission ratio (ER) calculated from LAFTIR ground measurements is a factor of 3 higher than that from airborne measurements?

A2.1. The DCH4/DCO ER from the ground-based samples is more than 3 times the ER for the airborne samples. This is well within the variability we routinely observe for this ratio and it is common for the ER to CO to be higher for smoldering compounds during smoldering combustion. Speculation about the cause for this is possible, but hard to support. We know that CH4 is produced most strongly by glowing combustion (Yokelson et al., 1997), but CO is also a major product of glowing combustion. A major message of the paper is that we are still trying to characterize the full range of variability in fire emissions and we cannot yet assign all the variability to specific factors. To address this comment we have made the following addition:

P25270, L6: “Additionally, the ER(CH4/CO) calculated from LAFTIR ground measurements is a factor of 3 higher than that from airborne measurements, which is well within the variability that we routinely observe for this ratio (Burling et al., 2011). Rather than attempting to assign this variability to specific factors, our main goal was to use

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these data to help characterize the full range of variability in fire emissions. The fire-averaged. . .”

R2.2. Page 25280, Line 1-3: The sentence is not clear to me. What explains why the ground-based samples had lower EF(NH3) than the airborne samples? It seems to me that ground-based samples had higher EF(NH3) because of lower MCE and NH3 is emitted from smoldering combustion.

A2.2. The average of the ground-based EF(NH3) was higher than the average of the airborne EF(NH3), which were acquired at higher MCE, but the ground-based EF(NH3) were well below the EF(NH3) that would be predicted at the ground-based MCE using the regression line fit to the airborne samples. We don’t have fuel N measurements, but it is very likely that the ground-based samples were of smoke from fuels with lower N content than the fuels that produced the lofted emissions. Fuel N content can be more important than MCE in determining the emissions of N compounds as shown by Burling et al. (2010). Table 2 shows that 32 of the 36 ground-based samples were of woody material, which tends to be low in N content. On the other hand, foliage tends to be high in N and to burn by flaming to produce lofted emissions. To clarify these points we have modified the text as follows:

P25279, L24-27: -Original text: “Other factors besides MCE can affect ammonia emissions, the most important being the nitrogen content of vegetation. The nitrogen content tends to be lower in woody biomass (e.g. logs) compared to foliage (Susott et al., 1996; Burling et al., 2011).” -Revised text: “Other factors besides MCE can affect ammonia emissions, the most important being the nitrogen content of vegetation (Burling et al., 2010). The nitrogen content tends to be lower in woody biomass (which tends to burn by smoldering combustion) than in foliage (which tends to burn by flaming combustion) (Susott et al., 1996; Burling et al., 2011; Akagi et al., 2011).”

P25280, L1-3: -Original text: “this could explain why the ground-based samples (often of smoldering logs/stumps) had EF(NH3) that were generally lower than the airborne data regression relationship would predict." -Revised text: "this could explain why the regression line fit to the ground-based EF(NH3) (usually of woody biomass, Table 2) lay well below the regression line fit to the airborne EF(NH3) data."

R2.3. Page 25284, Line 21: Suggest delete "at the appropriate ER".

A2.3. That sentence and this topic are a bit confusing. We think the following modified version is more clear. -Original text: "When a sample was emitted before or after we were at the source, the fire-averaged ER is still our best guess at the appropriate ER to compare to the downwind NEMRs" -Revised text: "When a downwind sample was emitted before or after we were at the source, the fire-averaged ER is still our best estimate of the starting ER to compare to the downwind NEMRs"

R2.4. Page 25285, Line 26: I suggest also cite the study of Singh et al. (2010) that showed ozone production in fire plumes when mixing with urban pollution measured from the ARCTAS campaign. "Singh, H. B., Anderson, B. E., Brune, W. H., Cai, C., Cohen, R. C., Crawford, J. H., Cubison, M. J., Czech, E. P., Emmons, L., and Fuelberg, H. E.: Pollution influences on atmospheric composition and chemistry at high northern latitudes: Boreal and California forest fire emissions, Atmospheric Environment, 44, 4553-4564, 2010."

A2.4. We have added the citation to Singh et al. (2010) after the citation to Lee et al. on line 26 and included this paper in the references.

R2.5. Page 25285, Line 6-8: What are the ozone concentrations in the fire plumes and in background air? The excess CO mixing ratios in those plumes are relatively low as discussed on page 25283. Would this lead to a higher DO3/DCO ratio in this study than previous studies as shown in Figure 13?

A2.5. The O3 mixing ratios in the background air were 50-80 ppb as given on line 6 page 25275. The O3 mixing ratios in the plumes are initially very small (well below background) and then increase to 80-100 ppb after about an hour as discussed in lines

24-26 and line 28 on page 25275. For a well-mixed background and the time scales in this study (a few hours), the DCO is just an inert tracer to normalize for dilution. O3 and CO should dilute at the same rate so for instance, if DCO decreases faster, we expect that DO3 would also decrease faster. Thus, low DCO values should not force high DO3/DCO values. It is possible that rapid dilution could affect O3 formation rates via kinetic effects, but that is beyond the scope of this paper.

R2.6. Page 25287 and 25288: Should section 3.7.1 and 3.7.2 be section 3.8 and 3.9?

A2.6. We agree the section numbering was not quite right, but have opted to create a new section 3.7.1 about Ozone at line 3 page 25285 and then increment the numbering for methanol and formaldehyde to 3.7.2 and 3.7.3, respectively, in order to keep all the plume aging results under section 3.7.

R2.7. Page 25304, Table 1: Please describe what 'nd' means. A2.7. This symbol indicated that the date of the previous prescribed fire on the site was unknown to us. We have changed the symbol to "unk" and added footnote #1 at first use explaining that "1"unk" indicates that the date of the last previous fire on the site is unknown."

R2.8. Page 25325, Fig. 12: Do the regression lines include both Lagrangian and non-Lagrangian samples? The Figure only plotted regression lines for the 1 Nov and 8 Nov samples. How about 7 Nov and 10 Nov? Are they not statistically significant? A2.8. We have changed the figure caption to clarify this. -Original text: "The y-intercept of the trendlines is forced to the average DO3/DCO NEMR at time t =0 h for each given fire." -Revised text: "The y-intercept of the trendlines for 1 and 8 Nov is forced to the average DO3/DCO NEMR at time t = 0 h for each fire. All trendlines represent only pseudo-Lagrangian data points. The 7 Nov data did not have enough points to constrain a line and the 10 Nov data was clearly non-linear."

In addition, to responding to the Referee's comments, we made the following minor, voluntary changes.

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P25274, L11: We changed “In light of the above fuel-specific observations,” to “In light of the platform-specific tendencies noted above,”

P25281, L22: We added “in NC” after “measurements”

P25282, L16-22: We made this a new paragraph and reorganized slightly: - Original text: “We also observed dimethyl sulfide emissions and report EF(DMS) of 0.032±0.040 (ground-based) and 0.008±0.003 (airborne). Dimethyl sulfide has a much shorter lifetime (∼1 day, Lenschow et al., 1999) compared to OCS, and is quickly oxidized to compounds like SO2 during daylight hours. Simpson et al. (2011) report EF(DMS) of 0.0023±0.0012, which is significantly lower than what was observed in this work. Like the OCS data, we note strong negative correlation with MCE (Table 4), confirming emission of DMS from smoldering and RSC.” -Revised text: “We also observed dimethyl sulfide emissions. Dimethyl sulfide has a much shorter lifetime (∼1 day, Lenschow et al., 1999) compared to OCS, and is quickly oxidized to compounds like SO2 during daylight hours. We report EF(DMS) of 0.032±0.040 (ground-based) and 0.008±0.003 (airborne). Like the OCS data, we note strong negative correlation with MCE (Table 4), confirming emission of DMS from smoldering and RSC. Simpson et al. (2011) report EF(DMS) of 0.0023±0.0012, which is significantly lower than what was observed in this work.”

P25283, L17-18: We changed “an excess CO” to “a DCO” where "D" indicates the "del" notation.

P25286, L13: We changed “such as terpenes” to “or particles” – (this adds an important possibility and eliminates what may be confusing since we earlier said that O3 would not be a major oxidant of terpenes until later in plume aging.)

P25286, L18: We deleted “of CO”

P25289, L24: We inserted “up to” before “97”

Table 1: Under the “Fuel Description” column, the “Francis Marion” entry has been

changed from: “Longleaf pine wire grass (Francis Marion)” to “Longleaf pine, wiregrass”.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 25255, 2012.

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