

We'd like to thank Referee 1 for their helpful comments, which are found in italics below. Our responses to each point are provided inline and the manuscript has been revised accordingly.

#### Specific Comments:

*Page 3864; Lines 2-5: The authors should use the updated and recommended rate coefficients as mentioned on the IUPAC website for calculating the lifetimes of the gas phase species with OH, in case the rate coefficients have changed compared to the Atkinson 1994 reference, which they have used. Also, if OH measurements were made during AMMA then why not use the measured OH concentrations for the lifetime calculations?*

The reference has been updated to R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, 2006, Atmos. Chem. Phys., 6, 3625-4055.

The manuscript has also been updated to include the statement:

“This estimate for average [OH] is consistent with the slightly higher range of daytime [OH] measured during flights on the BAe-146 (Commane et al., 2010)”

*Section 2.2, PTR-MS: Please mention the drift tube pressure and temperature at which the instrument was operated. Information should be provided about the type of sampling inlet (e.g. forward or reverse facing etc..) and sampling system or at least a citation to it if it has already been described elsewhere.*

This section has been revised to include the requested details:

“A pressure-controlled inlet allowed us to maintain a constant pressure (between 2.2 and 2.4 mbar) in the drift tube while making measurements up to an altitude of 9500 m. The drift tube field strength (E/N) used for the observations was 105 Td and the temperature was controlled at 313K.”

“The PTR-MS drew air from a forward-facing starboard air sampling pipe shared by the O<sub>3</sub> and NO<sub>x</sub> instruments. Zeros were carried out periodically in-flight by diverting the sample air stream for a period of 1-2 minutes through a custom-built stainless steel tube filled with a platinum-coated quartz wool catalyst (Shimadzu) continuously heated to 400 °C.”

*Page 3866, Lines 10-18: What was the range of humidity range covered in the laboratory based variable humidity calibrations? Note that Equation 1 assumes a linear correction, and humidity dependent sensitivity curves are not always linear between 0 and 90% RH (e.g. Sinha et al., IJMS, 2009). Thus, it would be good to mention the estimated error due to this effect alone considering that you encountered very variable humidity during the measurements (extremely dry at 9 km and quite humid in the lower troposphere).*

Our humidity-dependent calibrations were carried out at eight different relative humidities between 0 and 80 % RH. While the abundance of the water cluster at  $m/z = 37$  did not scale linearly with RH, we were able to produce abundances of  $m/z = 37$  ranging from  $2.5 \times 10^5$  cps to  $3.7 \times 10^6$  cps. We used the abundance of  $m/z = 37$  rather than the RH itself to derive of  $X_r$  factors. We were able to cover the full range of water cluster abundances encountered during the AMMA flights and thus we do not believe that extrapolations related to humidity-dependent calibration factors dominate our uncertainty. The last part of the paragraph has been reworded to reflect this:

“During AMMA the average value of  $i[\text{H}_3\text{O}^+]$  was  $6 \times 10^6$  counts per second, and  $i[\text{H}_3\text{O}^+\text{H}_2\text{O}]$  varied strongly as a function of absolute humidity ranging from  $2 \times 10^5$  and  $3 \times 10^6$  cps. The laboratory humidity calibrations covered the same range of  $i[\text{H}_3\text{O}^+\text{H}_2\text{O}]$  that was encountered during the flights. For the compounds discussed in this paper, the  $X_r$  values were 0.71 for acetonitrile, 0.09 for benzene, 0.68 for acetone, 0.85 for isoprene, and 0.79 for MVK+MACR.”

*Page 3868, Lines 2-5: For methanol both sampled ambient air and “zeroes” were reported to have strong altitude dependence. Previous measurements over the tropics by Eerdekens et al., 2009, which the authors cite, did not seem to have such a problem for methanol, so this does appear strange. Could the authors at least speculate why their PTR-MS system was unable to measure methanol reliably? Based on the high backgrounds observed at other  $m/z$  signals, I am concerned that their scrubber which was heated only for a minute (see Line 2, Page 3866) may not have been working well.*

The original sentence describing how zeros were carried out was poorly worded and has been revised (see above). The catalytic scrubber was continuously heated to 400 C, and the 1-2 minute period refers to the times during which the valves were switched to divert the flow past the scrubber. The catalytic scrubber proved effective at removing methanol from the sample stream in the lab and in the aircraft on the ground. The ambient signal for methanol during flight was always higher than the signal through the scrubber, but both types of signals had strong altitude dependencies. Because the cause of this dependence could not be understood, it was decided not to report methanol mixing ratios. The description of the data reduction in Eerdekens et al., 2009, does not suggest that the authors encountered the same issue. High background signals at  $m/z$  93 and 107 (xylenes) have been a chronic issue for this particular instrument both in lab and on the aircraft.

*Page 3869 and 3870: The authors have done a very good job in capturing the contrasting VOC signatures over different land use types (e.g. Sahel desert, forest, urban city etc..). However it is difficult to register this quantitatively from the Figures in the manuscript. Perhaps you could add a Table showing the average and std dev over these different land use types and the ocean for the VOC measurements done within the boundary layer.*

The following has been added to the paper, along with a paragraph in Section 3 expanding on the contrast between surface types:

Table 1. Average mixing ratios ( $\pm$  one standard deviation) measured below GPS altitude of 700 m over different surface types. The Sahel region encompasses measurements north of 13.8 °N, the mosaic forest between 7.2 °N and 13.1 °N, and the ocean south of 6.4 °N. Lagos air is selected from a single flight (B229), specifically when the aircraft was downwind of the urban area. Air considered to be influenced by Niamey was encountered shortly after takeoff and before landing on several flights, in the region between 13.1 and 13.8 °N and between 1.9 and 2.4 °E.

Compound	Sahel Desert	Mosaic Forest	Ocean	Lagos	Niamey
Acetone (ppt)	$1055 \pm 129$	$1001 \pm 233$	$485 \pm 178$	$1128 \pm 564$	$1183 \pm 259$
Acetonitrile (ppt)	$144 \pm 37$	$144 \pm 42$	$133 \pm 38$	$160 \pm 50$	$146 \pm 45$
Benzene (ppt)	$25 \pm 35$	$98 \pm 60$	$46 \pm 50$	$264 \pm 244$	$95 \pm 105$

Isoprene (ppt)	$-9 \pm 47$	$604 \pm 546$	$-3 \pm 45$	$418 \pm 273$	$67 \pm 114$
MVK+MACR (ppt)	$8 \pm 32$	$388 \pm 245$	$2 \pm 47$	$433 \pm 280$	$133 \pm 167$
CO (ppb)	$99 \pm 10$	$143 \pm 20$	$119 \pm 13$	$181 \pm 58$	$131 \pm 30$
O <sub>3</sub> (ppb)	$42 \pm 4$	$22 \pm 6$	$27 \pm 5$	$26 \pm 9$	$31 \pm 11$

*Page 3872, First paragraph: The discussion about why biogenic VOC are not expected to impact ozone production significantly in the upper troposphere is not clear to me. The authors should explain this point more clearly.*

The following information has been added: “The chemical tendency of ozone in these VOC-enriched airmasses will depend strongly on the abundance of NO<sub>x</sub>, which may be influenced by convective lifting of surface emissions or by lightning associated with the MCS. In the case of this flight, no enhancement of NO<sub>x</sub> was observed in the detrainment layers and thus enhancements in photochemical ozone production are not expected. In fact, ozone in these detrainment layers is significantly lower than most upper tropospheric ozone values, due to strong deposition to the forest surface with which it was recently in contact.”

*Page 3877, Lines 1-4: The authors mention that they did not see enhancements in acetonitrile while sampling urban air in spite of widespread biofuel combustion in Lagos and Niamey. How do they reconcile this?*

To our knowledge, there have been no measurements of acetonitrile emission rates from biofuel combustion. A recent paper from Christian et al., 2010, indicates that the emission ratios of HCN/CO are much lower from biofuel burning than from biomass burning, suggesting that acetonitrile emissions would also be lower. The following sentences have been added to the paper:

“Figure 7b shows a scatterplot of acetonitrile against CO for the Lagos data on Flight B229, and from the data collected on several flights in the lowest 700 m in the vicinity of Niamey. The slopes for these ratios are much smaller in urban air compared to biomass burning, and the levels of benzene tend to be higher. While no measurements of acetonitrile emissions from urban biofuel burning have been carried out, the low HCN/CO emission ratios observed from these fires (~0.5 ppt/ppb) suggest that acetonitrile emissions are likely small (Christian et al., 2010). The slopes in Figure 7b ( $0.32 \pm 0.07$  ppt/ppb for Lagos and  $0.7 \pm 0.1$  ppt/ppb for Niamey) are higher than the value of 0.1 ppt/ppb observed by de Gouw et al. (2003c) in Los Angeles, but because of the pervasive nature of the biomass burning outflow in the West African region, it is possible that these slopes may not exclusively represent emission ratios for biofuel or other urban combustion.”

*Figure 7: Below the regression line there are a number of points (coloured squares showing high values for benzene, low acetonitrile and high CO) that seem to keep completely off from the rest. Can the authors clarify why?*

These points represent the observations influenced by urban emissions from Lagos (the area marked with a dashed box in Figure 6). The points were not included in the fit given in Figure 7. In the revised manuscript the data from Lagos have been moved to Figure 7b and combined with data from Niamey to separately highlight urban data. See added paragraph above.

*Suggestions that the authors may want to consider for gleaned more information from their novel dataset:*

We appreciate the referee's suggestions for extracting additional insight from the observations, however after exploring their ideas, we don't believe much more significant analysis is possible:

*1) The authors suggest that the main reason for low ozone over the forest is its dry deposition to the forest. Can they also provide an estimate of the magnitude of this flux, based on the ozone levels over the forested and non forested regions that they sampled, the forested area and the ozone vertical profiles?*

While the decreases in ozone are often coincident in time and space with enhancements in biogenic VOC, it is not straightforward to convert this information into deposition fluxes of ozone. The regional budget of ozone has already been addressed in other publications using aircraft observations from AMMA. Saunio et al., 2009, used a deposition velocity of  $0.65 \text{ cm s}^{-1}$  for ozone over the forest in 2D Meso-NH model and demonstrated good agreement with observations. A model run without this deposition had almost 10 ppb more ozone than observations.

*2) With 85 hours of flight time over this region (well done) the authors would have sufficient data to construct diurnal profiles of some of the VOCs such as acetone and isoprene over the land and ocean within the boundary layer and overlay them. Note such information is obscured in Figure 6 and considering that the authors have kept the manuscript concise, an extra Figure would hardly be an issue.*

Due to logistical constraints, the data in the marine boundary layer was collected only in the middle of the day, so no diurnal profile is possible. Almost all of the flight hours focused on the characterization of the boundary layer took place during the day, and the latitudinal variability is much more significant than the diurnal variability. Over the forested region, we sorted observations below 700 m GPS altitude and between 700 and 2000 m GPS altitude. There is no clear diurnal cycle in the acetone observations in either of these altitude ranges. Isoprene tends to be higher during daylight hours, though elevated levels were also seen in the early morning hours, likely as a result of emissions from the previous late afternoon persisting in the residual layer. We believe the additional value provided by these figures is minimal and thus they are not worth including in the revised manuscript.

*Technical comment: In the reference list, Marandino et al., 2005 and Marandino et al., 2006 refer to the same citation which must be an error.*

In fact, the references refer to the original paper and a published correction. The reference have been corrected.