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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Technical Note: Characterisation of a DUALER instrument for the airborne measurement of peroxy radicals during AMMA 2006" *by* D. Kartal et al.

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Anonymous Referee #1 Received and published: 28 October 2009 1. In section 2.2 the authors state that a correction of the chain length due to humidity is not required under the conditions encountered during AMMA, as Tambient < Treactor and Pambient > Preactor, and they reference a Ph.D. thesis (Kartal, 2009). Ph.D theses are not always the easiest to get hold of, and without having read it I don't follow why this is the case. It would be useful here to add a couple of lines explaining this. Also, are the inlet systems heated at all? If they are, (and given the use of the pre-reactor),is Tambient < Treactor and Pambient > Preactor not always true, and not just under AMMA conditions? How

does humidity affect the chain length under other conditions? The dependency of the CL on the humidity has been thoroughly investigated at the IUP-UB. The CL decreases with relative humidity, and follows a function which varies depending on the shape and material of the reactor and on the [CO]/[NO] ratio of the gases added for the chemical conversion. This dependency has been characterised experimentally at the IUP-UB by Reichert et al., JGR 2003 (in the list of references) as you can see in the = f (RH) below for 20 and 30°, CLwet being the CL for 3%<RH< 90% , and CLdry the CL obtained at 3±0,5 %

The DUALER inlet was not heated during the AMMA flights. However, as its inner part, and therefore the outer part of the reactors, was connected to the cabin of the aircraft, the temperature of the reactors was always higher than the temperature of the sampled air. This temperature was regularly controlled and documented. The relative humidity is defined as . At pressures below 700 mbar, the difference in temperature between ambient air and reactors is high and the increase in in the reactors dominates the RH decrease. At lower altitudes, i.e., higher pressures, the decrease in the RH relative to the ambient is dominated by the decrease in the as the DUALER operates at 200 mbar. On page 18276 line 23 the text has been changed as follows:

"The DUALER inlet is not heated during the AMMA flights but its inner part is connected to the cabin of the aircraft. As a consequence, the temperature of the reactors remains always higher than of the outside air. Therefore, the RH, being , decreases in the reactors respect to the ambient as Tambient<Treactor causes the increase in and Pambient > Preactor causes the decrease in the in the reactors (Kartal, 2009)". 2. In section 3.1 the authors note that the NO2 detector sensitivity degrades along the experimental series, and explain that this is due to filter ageing. This would seem to be rather a rapid phenomenon – how often are the filters changed and could this affect the measurements performed over the course of a flight? The detector filters are changed before each flight. The filter ageing is a slow phenomenon observed during long series of measurements in the laboratory after a few days of continuous measure-

ments. There is no indication that this occurs over the course of a flight. The sensitivity changes observed during the flights are attributed to fluctuations of the luminol flow through the filters. 3. In section 3.3 the authors present the different eCL obtained for HO2 and CH3O2. It could be imagined that under the conditions present during AMMA many larger and more complex biogenic RO2 might be present. Do the authors have any thoughts on how the relative measurement efficiencies might vary for these? The eCL for a particular peroxy radical depends on: a) wall losses at the pre-reactor nozzle before the conversion into NO2 and amplification takes place. The efficiency of the wall losses is expected to be lower for larger organic groups but larger if a polar group such as OH or =O is present. b) chain length of the amplification cycle inside the reactors. As this cycle is initialised by HO2, this depends on the yield of the conversion to HO2, which is determined by the reactions:

Both a) and b) have to be characterised for each set up and measurement conditions (NO and CO concentrations, material and shape of the reactor). Ashbourn et al.(Journal of Atmos. Chem, 29, 233-266,1998) investigated the yields of HO2 reaching the amplification zone for their PerCA instrument and for the most common atmospheric peroxy radicals, taking into account the chemical and heterogeneous losses in their reactor:

Peroxy radical HO2 fraction reaching amplification zone HO2 0,69±0,05 CH3O2 0,78±0,05 C2H5O2 0.96±0,07 neo-C5H11O2 1,00±0,07 HOCH2CH2O2 0,73±0,05 CH3CH(OH)CH(O2)CH3 0,81±0,06 (CH3)2C(OH)C(O2)(CH3)2 0,83±0,06 CH3(=O)O2 0,78±0,05 Despite the different characteristics of the reactor used in this work, mainly affecting the heterogeneous losses, these values can be used as a reference to estimate the relative response to different peroxy radicals. Within AMMA there was no information about the peroxy radical speciation. HO2 and CH3O2 are the most likely peroxy radicals to be expected in the air sampled and the laboratory characterisation presented in the manuscript indicate that for the CH3O2 abundancies expected the peroxy radical mixing ratios can be between 8% and 14% overestimated.

This is in reasonable agreement with the results of the table above (3-7%) provided the differences in the corresponding set ups. 4. In equation 10 the mean values of the calculated sensitivities (ADet and BDet) for a particular time period are used, rather than the individual values of a(k) and b(k). What variability is typically seen in these values? If the detector sensitivity were to change midway through the period, would there be any advantages to using different averaging periods? The sensitivity of the detectors changes during the flights due to undesirable fluctuations in the luminol flow. These fluctuations lead to different values of ADet and Bdet , whose relative accuracy typically vary between 15-30% and 5- 15% respectively. If the sensitivity changes midway through a period, i.e., a pressure level, a new interval is indeed defined to obtain new more accurate parameters for the detectors. The text has been extended at the end of Sect.4.1.: “Within AMMA the ADi parameters obtained from the O3 in-flight validation generally varied between 15 and 35 with 15-30% relative accuracy, in reasonable agreement with the “a” parameters obtained in the laboratory, which varied between 10 and 30 with 3% accuracy” 5. Could the authors expand on what causes the measurement of negative RO2 concentrations in figure 15? Generally, very short term changes in the O3, NOy and NOx mixing ratios are associated with lower accuracy in the determination of the peroxy radical concentration as they introduce interferences in the calculation of the ïĄĎNO2, i.e. NO2 total- NO2 background, and also with lower accuracy in the effective calibration parameters calculated on the basis of the ozone measurements of the DLR-Falcon. On the 11 August there seems to be a change in the air mass sampled within the 450 mbar level as indicated by the sudden variation of all trace gases measured: O3 decreases about 10 ppb, while CO and NOy increase significantly. This can disturb the local chemistry and lead to short term variations in the background concentrations which can then result in negative RO2* values. These negative values are not removed from the data set since they provide information about the response of the instrument in the case of a rapid changing background.

On page18290 (Sect.4.3) line 1 the text has been extended for clarification: “In the first

two levels at 360 and 450 mbar, total odd nitrogen (NOy), O3 and CO change abruptly indicating the chemical inhomogeneity of the air mass sampled. This situation disturbs the local chemistry and leads to short term variations in the background concentrations which can then result in the calculation of RO2* negative mixing ratios. Spite being chemically meaningless these negative values are not removed from the data set as they are not caused by instrument failures and provide useful information about radical variability and instrument response in such a rapid changing environment. The analysis of data is however based on periods of stable conditions". Minor points: 6. Page 18273 lines 1 and 2 (and possibly elsewhere): "amount" is not a good word, "concentration" would be better here. The sentence has been accordingly changed. 7. Page 18273 line 14 would read better without the first "The", and "measurements" should be singular. Both sentences have been accordingly changed; 8. Page 18278 line 22: "till" should be replaced by "until the". The sentence has been accordingly changed 9. Page 18290 line 5: "which spite of their chemical meaningless" would better read as "which despite being chemically meaningless". See answer question 5. 10. The labelling of figure 3 is not clear (especially item labels 1 and 3), and I cannot find item label 4 on the figure at all. Most of the figures have been changed (see answer to referee 2)

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/9/C10975/2010/acpd-9-C10975-2010-supplement.pdf

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