**Atmospheric
Chemistry
and Physics
Discussions**

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Comment

Interactive comment on "Total OH reactivity measurements in Paris during the 2010 MEGAPOLI winter campaign" *by* C. Dolgorouky et al.

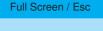**C. Dolgorouky et al.**

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At first we would like to thank both reviewers for the careful reading of our paper and for their valuable comments and suggestions which help improving the quality of the manuscript. Hereafter we answer point by point to the different comments.

Comments from Referee #1

Specific comments

1. Since the correction factors by NO and water vapor are very large (Fig.3, 4), even the author checked the influence of NO and water contents in laboratory, readers would

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wonder if the correction can be applied for the urban ambient air measurement properly. Is it possible to show the correction by NO and water vapor in real polluted ambient air? Large OH reactivity around 120 s-1 is possible in polluted urban air. But the period 3, NO (and other typical pollutants) was not high and the air seems to be not very polluted.

1/ The major concern of referee 1 is linked to correction factors by NO and water content. We agree that these corrections are large and that in future measurements, some improvements should be made to reduce these uncertainties. The correction factors which were applied for RH and NO corrections were determined on the basis of experiments which were directly performed on the field and not at the laboratory. Nevertheless, the referee is right to underline that these experiments were not performed with the real polluted air (because it was too much variable and could not be used for tests) but with controlled air. Nevertheless we have some arguments (see below) indicating that the main conclusions of the paper (high missing reactivity during periods of continental air masses) are robust despite these corrections. The referee underlines that period 3 is associated with high level of OH reactivity but with low levels of NO which seems to indicate that the air was not very polluted. We agree that the local pollution due to primary pollutants was low during this period (as shown by low levels of NO, a tracer of local pollution due to its short lifetime). However, the high aerosol loading during period 3 do suggest a high level of polluted air, mainly composed of secondary compounds. As this period 3 was associated with low levels of NO and therefore with a weak correction due to NO for the OH reactivity, it suggests that the high levels OH reactivity observed (>120 s-1) were real. Note that during the whole period III, the correction due to RH had globally lowered the OH reactivity (by 30% on average). In addition, following the referee's suggestion, we have now plotted the benzene/toluene ratio which shows a co-variation with the reactivity, confirming that during period III old polluted air was sampled. This point has now been added in the revised manuscript (see our answer to the last comment of the referee).

2. Possible error is discussed in the text. But the error is not liner for the OH reactivity

deduced by CRM from equation (1). Is it possible to show error bar (not data deviation, but theoretically deduced error) in some figures?

2/ We agree with the referee that the error is not linear and only a first approach of error examination is given in the paper (as described page 10946 line 10-16, page 10949 line 22-28). In order to show estimated uncertainty on the results we have added errors bars in figure 7 (now figure 8). However, in order to not lower the clarity of the figures, we have chosen to show only errors bars for three different points corresponding to low, medium and high values of reactivity which shows the expected level of uncertainty and which also shows the non-linearity of the error. For clarification, we have also now added in the legend of Figure 2 (now Figure 3) the meaning of the shown error bars "Error bars stand for estimated uncertainty on the measured and calculated OH reactivity (see text)."

3. Page10944 line 25: Did you check the influence of filter with your system? The referred paper was using different technique. In 3.4 and Fig. 12, you mentioned relationship between missing OH reactivity and SO4, NO3, NH4 (and organic aerosol).

3/ We did not check the influence of the filter on our system but we would like to underline that the referred paper was used to disregard the influence of the inlet system on the atmospheric OH reactivity and therefore the technique employed to measure the OH reactivity does not play a role here. We believe that the relationship we mentioned between missing OH reactivity and aerosols (organic and inorganic) for some periods is due to high loading of pollutants during these periods. If this relationship was due to a measurement artifact, all increases of aerosols would lead to increases on OH reactivity, which was not always the case (see for example on figure 12, February 4 when a small event on aerosol was clearly observed whereas the OH reactivity stayed almost stable or early February 1 when reactivity OH increases whereas aerosol decreases). Moreover, the relationship between missing OH reactivity and aerosols is also seen on the benzene/toluene ratio (see last point from the referee) and therefore tends to rule out the hypothesis of an artifact.

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4. Page 10947 line 16- : Was the relative humidity (RH) of the ambient air you mentioned here at chamber (24 C), or reaction chamber of PTRMS, or ambient temperature? If RH was at ambient air temperature, RH will change at reaction chamber of PTRMS or in the laboratory (24 C). In my understanding, the influence of water vapor on PTRMS signal will be depending on absolute water concentration in the reaction chamber of PTRMS. In your system, the chamber (room air) was kept 24 C, and T (should be 24 C) and RH were monitored at the end of the chamber, and also water vapor in the PTRMS chamber was monitored by water cluster signals. Therefore RH and water concentration will be proportional. I believe authors consider these differences properly. But it is not clear in the text when you say RH (where the RH is measured).

4/ The referee is right, the text was not precise enough concerning the RH. The relative humidity which was mentioned page 10947 line 16 was the one measured in the atmosphere (at ambient temperature), therefore slightly different from the one which was measured at the exhaust of the chamber at 24°C. To avoid confusion, the corresponding sentence has been deleted in the revised manuscript and therefore when RH is mentioned it only means RH measured at the exhaust of the reactor (24°C).

5. Page 10963 line 1-4 : HCHO is one of important OVOC, and its contribution to total OH reactivity would be 5-10%, and be more important in clean atmosphere. Is it possible to estimate HCHO concentration? For assume HCHO and CH3CHO is proportional etc.. This have also problem, but better than without consideration in fig. 10, 11 etc.

5/ As mentioned in the paper (P 10963, L1-3), we have performed calculations considering high values of formaldehyde (10 ppbv) but the equivalent OH reactivity was low (only 2 s-1) and therefore the impact of formaldehyde was not further used and discussed in the manuscript.

6. Page10963 line 8-9 : During February 5-8, what kind of interferences were ex-

pected?

6/ Possible interferences include water droplets and pyrrole desorption (the pyrrole being very sticky, sometimes desorption of pyrrole has been observed, leading to a short perturbation in the system). This is now indicated in the revised version of the manuscript.

7. Figure 9 : During period 3 (February 9 - 13), observed OH reactivity had clear diurnal variation (OH reactivity were high during nighttime?). Do you have any explanation about this? From the calculated OH reactivity (red line in Fig. 9), there were not such diurnal cycle.

7/ The calculated OH reactivity presents a weak diurnal cycle which mostly follows the diurnal cycle of the compound contributing mostly to the calculated OH reactivity (i.e. NO2). During the period 3 (February 9-13), the calculated OH reactivity presents the larger peaks in the morning. These are due to the influence of traffic emissions on NO/NO2 (and therefore on OH reactivity). We note that during this period, the calculated OH reactivity also shows small nighttime peaks (except during the night from February 8 to 9), also associated with NO2 peaks. We attribute this nighttime peak to a lower boundary layer height during the night. Nevertheless, the calculated OH reactivity increase observed during the night is very much lower than the one observed on measured OH reactivity (10 s-1 on the most versus more than 60 s-1). We do not have yet a satisfying explanation for these high nighttime values during period 3. Nevertheless the fact that the independent measurements of benzene/toluene ratios (see last comment) and of inorganic aerosols show as well such a diurnal cycle with higher values during the night suggest this is a real phenomenon. We have included a short paragraph to comment on that point in the revised version of the manuscript. "One striking feature is that the missing reactivity presents the same diurnal cycle as the benzene/toluene ratio and as the inorganic aerosols during period III with values higher during the night. We do not have yet a satisfying explanation for this diurnal cycle but the fact it is presented for three independent parameters (inorganic aerosols,

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benzene/toluene ratio and missing reactivity) suggest that is was a real phenomenon, maybe linked with the dynamics of the atmosphere".

8. Figure 10 and 11 : It will be useful information to show the average total OH reactivity values in these figures (and text).

8/ The information requested by the referee (the average total OH reactivity values) were included in the text of Figure 10 and 11 (for clarity it was not included in the figure itself).

9. Figure 12: For the explanation to show the aged polluted air, backward trajectories and AMS results (SO4, NO3, NH4) are shown. Is it possible to check the age of air by ratio of VOCs?

9/ We thank the referee for this very valuable suggestion. Indeed VOCs ratios can be used to estimate air mass photochemical ages and a typical ratio used is benzene/toluene as these aromatic compounds have similar sources but different reaction rates with OH (toluene being about 5 times more reactive). Plotting this ratio with the missing reactivity indeed shows that all peaks with high values of missing reactivity (>20s-1) are associated with high benzene/toluene ratio (>1) whereas when the OH missing reactivity was low (<20 s-1), this benzene/toluene ratio was lower (<1). For the period III (8-13 February), the benzene/toluene ratio peaks at the same time than the missing reactivity (nighttime), which confirms that this episode was associated with aged polluted air. A paragraph commenting on this new feature has now been added in the revised manuscript. "Figure 13 shows as well the evolution of the benzene/toluene ratio. This ratio has been largely used in the literature (following the initial idea of Roberts et al., 1984) to estimate the age of an air mass as these two aromatics compounds are usually issued from the same source whereas their reaction rate with OH differ by a factor 5. Therefore a low benzene/toluene ratio will suggest a fresh pollution whereas a higher value will suggest an older pollution. Figure 13 shows that the highest values of the benzene/toluene ratio were observed during period I and III con-

firming the sampling of air masses impacted by aged pollution at that time. We note that one very high value of the ratio was also observed on January 24 but this was due to a high peak of benzene which may have been caused by a local specific source. "

[Technical corrections]

Page 10940 line 10 : The most important difference between the measurement methods are not "produce OH", but "detect the decrease of OH".

Page 10945 line 25 - : Unit of reaction rate constants will be "cm3 molecule-1 s-1". (without "s" in molecule). (page 10948 line 13,)

Page 10946 line7 : It should be clearly indicated "facsimile" is the name of the model calculation.

Page 10952 line 12 : "HR" -> "RH"

All technical comments have been taken into account

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 10937, 2012.