

## ***Interactive comment on “Total OH reactivity measurements in Paris during the 2010 MEGAPOLI winter campaign” by 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 #2

Discussion points

1. P10939 ‘Generally, the production processes for OH are relatively well understood’ – I am not sure that this is the case and it would certainly be worth citing a few references

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here. Ozonolysis can compete with O<sub>3</sub> photolysis as a source and in the complex urban environment, recycling processes may be important. This does not detract from the current measurements – if fact it makes them more important.

1/ We agree with referee 2 and we changed this part of the introduction accordingly. In the revised manuscript the sentence “Generally the production processes for OH are relatively well understood” has been changed with “Budget of OH radical is still associated with large uncertainty. Although the source term is generally dominated by ozone photolysis, additional OH sources can also be significant, especially in a urban environment, such as photolysis from nitric acid or from various aldehydes as described in details in Michoud et al (2012) and references therein. The lost processes, or sink tem, are also still poorly constrained”.

2. P10942 Need to provide a reference for the rate coefficient of OH + pyrrole. Have you tried using other compounds?

2/ A reference has been added for the rate coefficient of OH + pyrrole. No other compound was tried. Atkinson, R., Aschmann, S. M., Winer, A. M., and Carter, W. P. L.: Rate Constants for the Gas-Phase Reactions of OH Radicals and O<sub>3</sub> with Pyrrole at 295+/-1k and Atmospheric-Pressure, Atmos. Environ., 18, 2105–2107, 1984.

3. P10944 A figure showing the location of the measurement relative to the Paris conurbation would be useful.

3/ A figure presenting the Ile de France area and Paris conurbation and indicating the location has been added (Figure 2).

4. P10945 Have you performed any tests on the wall loss rates during sampling. A 35s residence time could be significant for low volatility compounds.

4/ As no wall tests were performed, we cannot completely exclude loss of low volatility compounds. Nevertheless, this effect would lead to an underestimation of the reactivity, which let the conclusions of the paper robust.

5. P10946 and Fig 1 – It is not clear from Figure 1 why pyrrole is photolysed. In Fig 1, it appears that UV generation occurs outside the main flow reactor. This seems a more logical way of setting up the apparatus. 20% photolysis could generate a significant radical concentration that could induce unwanted secondary chemistry – see also point 2, other reference compounds.

5/ The reactor is a turbulent flow reactor in which a flow of pyrrole + zeroair / ambient air of 200 sccm mixes in with 100 sccm of N<sub>2</sub> at the mixing site right after the respective arms of the reactor (e.g. see arm A and arm B of Figure 2; in Sinha et al., 2008 and Figure 1 of current work). While UV generation occurs within arm B, some rays from the Hg vapour lamp still enter the reactor, which is why a wood horn bulge was incorporated in the reactor design (see arm E of Figure 2, Sinha et al., 2008 and Figure 1 of current work). The pen ray Hg lamp has emission lines at 184.9 nm (which photolyzes the water vapour, but also at 253.6 nm. Pyrrole has been reported to absorb around the 253 nm wavelength (Bavia et al., 1976; Cronin et al., 2004) and hence photolyzes.

We have added in the revised version the following precisions in section 2.2.2. “Photolysis of pyrrole is one of the possible interferences. Indeed the reactor is a turbulent flow reactor in which a which a flow of pyrrole + zeroair / ambient air mixes in with N<sub>2</sub> at the mixing site right after the respective arms of the reactor (Figure 1). While UV generation occurs within the arm, some rays from the Hg vapour lamp still enter the reactor, which is why a wood horn bulge was incorporated in the reactor design (see arm E of Figure 2, Sinha et al., 2008 and Figure 1 of current work). The pen ray Hg lamp has emission lines at 184.9 nm (which photolyzes the water vapor), but also at 253.6 nm. Pyrrole has been reported to absorb around the 253 nm wavelength (Bavia et al., 1976; Cronin et al., 2004) and hence to photolyze.”

The point about secondary chemistry in the CRM reactor has been addressed in detail by Sinha et al. (2008), though it was not mentioned in the current work. Since the chemistry of pyrrole peroxy radicals and indeed of peroxy radicals formed from most hydrocarbon precursors is not well understood in terms of products (pyrrole peroxy +

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HO<sub>2</sub> ? k?) and only a few rate constants have been directly measured, the best way to investigate the influence of the net impact of all these radical reactions on the reactivity measurement was to conduct tests with complex mixtures of VOC standards and single VOC standards having rate constants ranging from  $k = 10^{-10}$  (e.g. isoprene) –  $10^{-14}$  (e.g. acetonitrile). This has been done extensively in the first paper on the CRM method (Sinha et al., 2008) and subsequent works by Kim et al., (2010), Noelscher et al., (2012) In all these tests the OH reactivity due to the VOC standard (s) could always be accounted for by the method within uncertainties. As reported in Sinha et al. (2008) the calibration line due to the 19 component hydrocarbon standard (containing VOCs such as acetaldehyde, hexanal and aromatics and methyl vinyl ketone, which absorb UV light and are introduced at concentrations of 7 to 17 nmol mol<sup>-1</sup>, 17 ppb of any VOC is very high considering typical ambient levels), falls on the same trend line as that of propane (Fig. 4 of Sinha et al., 2008), suggests that this is not a significant effect. A further test for secondary chemistry along the reaction length, and the sensitivity to slight change of flows (20 ml minute<sup>-1</sup>) the PTR-MS probe (inlet D of the glass reactor; Fig. 2) was placed at different points along the length of the glass reactor. However, no noticeable change in the measured pyrrole signal was observed. This simple test was also applied in the field, while sampling ambient air to investigate the influence of secondary chemistry within the glass reactor. The OH concentration measured using the C1-C2 signals of pyrrole is a net OH concentration (balance between fast production and loss processes). Our conclusion is that since the lifetime of OH radicals is less than 3 milliseconds within the reactor, the competitive kinetics of OH radicals involved in the OH reactivity measurement occurs too fast for secondary chemistry to compete on the same time scale.

We make a short comment about this in the text and refer to the papers which have investigated this effect. “No significant effect has been reported in previous studies from a potential secondary chemistry occurring in the reactor (due for example from radicals generated through the photolysis), as investigated in details by Sinha et al. (2008), Kim et al. (2010) and Noelscher et al. (2012)”.

6. P10948 Quantification of NO interference was been tested for by propane addition. Have you tried other hydrocarbons? Propane oxidation is straight forward, larger hydrocarbons where complex rearrangements can occur may produce a different result. What is the origin of the change in gradient in the NO interference plot?

6/ Unfortunately the NO interference was not tested with other hydrocarbons during the MEGAPOLI campaign. A test made later on with a similar reactivity system and using an isoprene standard (so much more reactive) has shown similar slope for the NO correction when NO was below 20 ppb (A. Noelscher, personal communication). Unfortunately during this test no measurement were performed for  $\text{NO} > 20$  ppb. As this later test has been performed by another group and as it did not allowed confirming the two slopes (because the test was performed for NO below 20 ppb), we choose to not mention it in the paper. Nevertheless, it gives a good confirmation for the correction which was applied during MEGAPOLI for  $\text{NO} < 20$  ppb (which correspond to 99% of the OH reactivity dataset). We have not identified the origin of the change in gradient in the NO interference plot.

7. P10950 GCFID measurements are taken from a different location and at a different timescale from the OH reactivity measurements. How does this affect your results?

7/ GCFID measurements were also taken on the roof of LHVP and the distance between the inlet of the sampling line of the GCFID and the inlet line of the OH reactivity system was only a few meters. In fact, all sampling lines from VOC instruments were on the roof of LHVP, within a few meters of the OH reactivity sampling line. This is now mentioned in the revised version of the manuscript (section 2.3) Due to the lifetime of the compounds measured by the GC-FID ( $> 1$  hour), we believe this small distance had no effect on our measurement. As the OH reactivity measurement and the different analytical systems had all different timescale resolution, we have chosen to average all measurements every 1.5h, which corresponds to the time resolution of the slowest instrument (GC-MS). Although this average does not make possible any analysis of very short term fluctuations, it still allows comparing measured and calculated OH reactivity

levels and variability.

8. P10955 CO values. The maximum values of CO in Paris, Tokyo and Mexico seem quite different and can't really be considered as 'similar'.

8/ We agree with the referee and have changed this in the revised manuscript. We now state that CO values are lower than in other megacities.

9. P10955-6 I think it would be useful to expand on the source inventory. I think this is very important in determine reactivity from local emissions and comparing with measured reactivity from other locations.

9/ We agree with the referee that it would be interesting to further discuss the source inventory as it may help a more complete discussion when comparing with other cities. However, this is not the scope of this paper which focusses on the first OH reactivity measurements performed in Paris and on the evaluation of the missing reactivity. Another paper is currently in preparation (Gros et al.) and will specifically examine the VOCs source contributions during the MEGAPOLI campaigns and will compare them with the source inventory. Therefore we have decided to not expand on source inventory in this paper but now we do mention the paper in preparation on this subject.

“The main primary emission source in Paris is considered to be the traffic activity which is confirmed by the results of a similar VOC source apportionment exercise performed for the MEGAPOLI campaign (Gros et al., in preparation for ACP). This study will allow further investigation of the role from local emissions on reactivity. “

10. P10966 I think the comparison with reactivities in different megacities is very difficult. OH reactivity measurements are by their nature a point measurement. OH reactivity is determined by local VOC concentration. OH reactivity in a busy street of a small town might be comparable with OH reactivity in a background location of a megacity. The subsequent section on the variation with atmospheric constituents is probably more relevant and interesting. Seasonal variations would also be interesting.

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Is there a correlation between the reactivity and missing reactivity with the age of an air mass from a given source (e.g. as measured by the Benzene:Toluene ratio)?

10/ We do agree with the referee that the comparison of the OH reactivity levels in Paris with measurements in other cities is a limited exercise and we do precise this at the beginning of this section. “One should keep in mind that comparing OH reactivities in different places is a limited exercise as they are by nature a point measurement which can be variable inside a same city. Nevertheless, the measurements performed during the MEGAPOLI campaign took place at a site where well mixed air was sampled and therefore could be considered as representative of Paris background air.”

As suggested by both referees, we have examined the missing reactivity according to the benzene/toluene ratio used as a proxy of the air mass age. We find a general co-variation between the missing reactivity and the benzene/toluene ratio, which is consistent with our hypothesis that high missing reactivity was associated with aged polluted air. We have added this very valuable point in our revised manuscript as well as a new version of figure 12 (now figure 13) showing the benzene/toluene ratio with the missing reactivity. “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 confirming 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 caused by a local specific source. “

After the paragraph commenting on the inorganic aerosol variability

“One striking feature is that the missing reactivity presents the same diurnal cycle as

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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, benzene/toluene ratio and missing reactivity) suggest that it was a real phenomenon, maybe linked with dynamics”.

## Minor Editorial notes

P10940 In the discussion of previous reactivity measurements refer to the tabulation in Table 4. In many ways these data would be better represented as a table or figure here.

P10941 Finland

P10943 Should be a small ‘k’ in equation 1?

P10953 Period III 9th Feb (not Jan)

P10957 Include photolysis lifetime for acetone?

P10972 References – check capitalization in titles of references.

All minor editorial notes have been taken into account

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

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