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Atmospheric Chemistry and Physics Discussions

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

P. Seakins (Referee)

P.W.Seakins@leeds.ac.uk

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OH radical concentrations are dominated by local chemistry and hence, unlike longer lived species whose concentrations are determined by a complex mix of chemistry, transport and primary production, provide a good test of our understanding of chemical mechanisms. Measurements of OH concentrations in complex chemical environments have recently been the subject of considerable controversy. Whilst much of the debate has focused on environments dominated by biogenic emissions, where measured OH concentrations have been up to an order of magnitude greater than models, OH generation mechanisms in urban environments are also uncertain. Additionally, concerns

have recently been raised regarding potential interferences in OH radicals. Given the uncertainty in OH sources and ambient concentrations, measurements of the total rate of OH removal are important to constrain at least one parameter. This paper reports OH reactivity measurements made by the Comparative Reactivity Method (CRM). A detailed description of the validation of the process in the field is provided, measurements of OH reactivity for an $\sim$3 week period of winter 2010 in Paris are presented and the results are compared with previous measurements in urban environments.

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 here. Ozonolysis can compete with O3 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.

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

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

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

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.

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?

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?

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'.

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.

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

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.

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