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Atmospheric
Chemistry
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Discussions

Interactive comment on “The Comparative Reactivity Method – a new tool to measure total OH reactivity in ambient air” *by* V. Sinha et al.

Anonymous Referee #1

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In this paper a new method for determining the rate of loss of OH radicals from the atmosphere by reaction with its sinks is presented. Such a measurement is very valuable, as it is never possible to measure all of the sinks that react with OH, despite advances in instrumentation in determining ever more complex VOCs. In this manner, one half of the budget of OH is obtained, and if the steady state approximation is used, the reactivity of OH can be multiplied by the OH concentration (if measured) to determine the production rate of OH. Several comparisons with models can now be made

(a) What fraction of the removal rate of OH is encompassed by the chemical mechanism used in the model, what fraction of sinks are missing? (b) Is the degree of missing sinks consistent with the agreement between measured and modelled OH

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radicals? Another way of putting this is whether the production rate of OH is faithfully represented by the model.

Measurements of OH and its reactivity therefore provides a more in depth analysis of the understanding of the fast photochemical cycles in the troposphere, as one can point to deficiencies in production or loss terms in the OH budget (or even both). There are many examples in the literature of striving for perfect agreement with measured OH, using models that are clearly deficient (e.g. constrained with very limited number of sinks, or using -lumped-; mechanisms), often both in the sources and sink terms in the chemical mechanism used. Cancellation of missing sinks and missing sources can lead fortuitously to good agreement between measured and modelled OH, and conclusions that the chemistry is well understood are wrong. Reactivity measurements enable the sink part of the model to be evaluated, and when combined with measured OH, it is possible to evaluate the accuracy of the production part of the model. This is a powerful combination.

Two other methods have been previously used to measure the OH reactivity (units of s-1, the inverse of the OH lifetime, in seconds), both relying of direct detection of OH using laser-induced fluorescence. In one method, the OH is made by photolysis of water vapour using a lamp in an injector, which is then exposed to ambient air for different reaction times before being detected, enabling a decay trace to be determined. In the other, OH is made by UV laser photolysis of ozone, which generates O(1D) atoms, which in the presence of water vapour produces OH. A second laser is used to detect the OH and the delay between the two lasers is increased in steps to measure the OH decay. This second method requires two laser systems. The former method has an added complication if air is used to make the OH, as HO2 is made concurrently, and even for production of OH in an injected flow of humidified N2 leaves H atoms, which once exposed to the ambient flow, will produce HO2. Recycling of HO2 to OH via reaction with NO in the added flow causes the OH decay rate to decrease, complicating the analysis, although a correction can be made if the concentration of NO, and the

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variation of HO2/OH with time is known. The ozone 2 laser method only makes OH, but the amount of OH will depend upon the amount of water vapour present, and the use of 2 lasers has associated problems, particularly in the field.

The development of a third method is therefore very welcome, as presented in this manuscript. A description of the instrument, some laboratory tests and a very brief flavour of some field performance is given in Mainz and a rainforest. No method is perfect, and it is clear that this method has some difficulties, some of which are common to the other methods, some unique to this particular instrument. The authors have summarised the previous work very well, have provided a detailed description of their instrument, and have been careful to point out the potential pitfalls of their new method, and provide details of experiments to quantify the effect of known interferences and known problems with the method; in order to enable some corrections. One is then able to quantify the uncertainty of the method, and under what conditions (e.g. here $<$ 5 ppb NO) measurements from the instrument are -valid-;. Such an approach is to be applauded, and reflects the background of the scientists concerned, which is firmly routed in the laboratory, where careful consideration of secondary chemistry and their kinetics, incorporating a simulation of the chemistry, are required.

The new method would seem to be ideally suited to a low NOx environment when the OH loss rate is quite high ($>$ 6 s-1), i.e. in a forest, and measurements of the reactivity are presented for a couple of hours in a south American rainforest. These are the first measurements of the OH reactivity in such an environment, and the lifetime of OH can be very short indeed, approaching a few milliseconds. It is a shame that more measurements were not made in the campaign, but there were instrumental failures and the PTR-MS instrument was required also for other duties. The instrument shows promise and I look forward to seeing more measurements in the future. The authors would like to intercompare their instrument with one of the LIF methods in the future, and I hope that this proves possible. The accuracy of the method can be checked by using a known amount of added OH sinks (and hence the reactivity can be calculated).

The method is a competitive method. The rate of removal of OH (generated artificially in the instrument) by its sinks in the atmosphere are compared with the rate of removal of OH by an added species, pyrrole, which is not present in the ambient air sample and is added artificially. The rate of OH removal is not measured directly, however, and this marks the difference with the other methods. When the ambient sample is not present to remove OH, the OH concentration is higher and therefore more pyrrole is removed and its concentration is reduced. When ambient air is introduced, some of the OH is removed by reaction with the ambient sinks, and the rate of pyrrole removal is therefore less, and its concentration is higher. A real time method with good time resolution (PTR-MS) is used to measure the pyrrole, and hence reactivity measurements with good time resolution are obtained.

The impact of this work is high, there are clearly significant missing OH sinks in the Suriname rainforest. The work will help to determine the scaling of OH sinks in models necessary to bring modelled and measured OH into agreement, and if combined with OH measurements (not done here but possible in the future) can help to constrain the production rate of OH in the forest. This environment, and details of the oxidative chemistry involving OH are central to our understanding of the global atmosphere. A good understanding of the chemistry, embodied by good agreement between measured and modelled OH, is central for predictions of global chemistry-climate models. The method does not necessarily need a PTR-MS to measure pyrrole, indeed any sink for OH not present in the atmosphere can be used (there are some caveats to the choice of sink, e.g. the rate coefficient for reaction with OH must be well known and sufficiently high, it must be easily handled and not be subject e.g. to significant photolysis by the light used to make the OH), and any suitably sensitive method can be used to detect the artificially added OH sink.

Subject to the satisfactory response to relatively minor points made below, I favour publication in ACP. The paper is very well written and presented.

Abstract. A very important aspect of the paper is the determination of possible inter-

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ferences which could complicate the determination of the reactivity measurement and lead to errors. Three of these are investigated later in the paper, (a) Photoylsis of pyrrole, (b) recycling of HO2 to OH, and (c) differences in humidity between sampled air and the zero air used to make the OH. These should at least be listed in the abstract, and a typical range of conditions where it works listed. For (a) what is the % error associated with this, for (b) what range of NO is the method OK up to in its present configuaration, and (c) that this is a problem but can be circumvented if they are kept similar. Without this, reading the abstract suggests that the method is free of problems, for example (b), which can cause problems with other methods. This is not the case. A fourth effect, namely the limitations of the instrument for low reactivities should also be stated in the abstract. Also, there is no indication of uncertainty in the abstract. There is a discussion on page 18 and the numbers should be stated in the abstract.

Page 4. Equation (2), need a square bracket around OH as it is a change in concentration with time.

Page 6, 3 lines below equation (3), again [OH] Equation (4), [OH]

Page 7, units of OH concentration are molecule cm-3, again on page 9., and on page 12, and elsewhere in the paper.

Page 8. End of paragraph 2, worth adding a sentence that the fate of the H atoms will be discussed later in the paper (I was left wondering about this).

Page 9, space after the reference after ... Werneke, 2007).

Page 12. The method is limited for reactivities $<$ 6 s-1. The method -lacks sensitivity-; for $<$ 6 s-1, and this is quantified a little further in the following paragraph. A comparison should be made here with the other methods, where there is less restriction for low reactivities (dependent though on NO), and measurements in lower reactivity air can be made with better accuracy. It is interesting that the limitation is controlled by the change in pyrrole concentration that can be made using the PTR-MS when the concentration is very low to begin with. The kinetic analysis in the following section is very interesting and shows that the authors have an in-depth understanding of the kinetics when the OH concentration is similar to that of pyrrole, and the assumption that pseudo-first-order conditions can be used in the analysis is no longer valid. There is no doubt that this is a complication of the method (and a mention ought to go in the abstract) but this is well understood.

Page 13. 3 lines from bottom. Does the slope of 0.79 after the correction then imply that the agreement with the expected reactivity (from the calibration) is worse than before the correction? But the point made is that the difference from 1.00 is within the uncertainties?

Page 15, reaction (R11), the rate coefficient above the arrow needs units

In common with other methods, HO2 recycling to OH is a problem when NO is elevated. At the end of P15 it states that the measured OH reactivity tends to zero at 10 ppb NO. Does this mean then that for polluted urban areas where NO can easily reach this value, that it is not possible to make reactivity measurements, as a correction cannot be made to such a reactivity? The simulations for 10 ppb show a correction from 16.5 s-1 to 5 s-1, which is quite a big change. I am pleased though to see that the issue of recycling to OH has been addressed properly via detailed modelling in this paper about OH reactivity measurements. Clearly measurements in urban areas where reactivities are high but also NO is high are going to be difficult. It would be worth a brief discussion of where (i.e. at which concentrations of NO) the other methods fall down. Measurements for example have been reported for New York city and also Tokyo where NO must be very high.

The humidity complication would not appear to be a major one as long as the zero air is humidified to a similar extent to that of the ambient air.

Page 18. The uncertainties for different reactivities given in the discussion on p18 should be stated in the abstract.

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Page 19. Ozone is generated at the ppm level, and this can react with pyrrole, but is shown to be a minor loss of pyrrole. Does the ppm level of ozone reacting with either OH or HO2 have to be taken into consideration? Also, for 1x10(12) levels of radicals, does one need to consider any OH+HO2 reaction?

Alternative methods for making OH is suggested which does not make HO2, namely H2O2 photolysis or N2O photolysis in the presence of H2O. For the former, H2O2 levels need to be low enough after photolysis that OH+H2O2 does not dominate the OH loss, and for the latter, H2O must be kept out of the N2O photolysis region unless careful filtering of the lamp radiation is used.

Page 21. It is perhaps worth differentiating the two LIF methods of Ren et al and Sadanaga et al.

The figures are of fairly good quality. The writing is too small in several instances, e.g. on the legends and on some of the plots. The size of the symbols should also be increased on some of the plots.

Figure 10. Say more explicitly which species are included in the calculations of the OH reactivity (which isoprene oxidation products). Clearly, in the future more measurements in such an environment over a diurnal profile will be most revealing.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 18179, 2007.