

Interactive comment on “A flow-tube based laser-induced fluorescence instrument to measure OH reactivity in the troposphere” by T. Ingham et al.

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I wish to compliment the authors for the development and characterization of their new LIF based field instrument for direct measurements of the atmospheric sink of the most important atmospheric oxidant, namely the hydroxyl (OH) radical.

As pointed out by the authors direct measurements of the total OH sink (also called OH reactivity) are necessary for a correct understanding of the oxidizing capacity of the atmosphere as they enable us to test whether we measure and account for all the ambient air sinks of the hydroxyl radical during atmospheric oxidation and emission studies. Direct measurements of ambient air OH reactivity were first made possible by

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Prof. Brune's group in 2001 (Kovacs et al., 2001), and it is a testimony to the analytical challenge such measurements represent, that even today only 5 research groups all over the world have made such measurements in ambient air and we continue to have a rather sparse dataset on directly measured OH sinks from different environments in the literature.

I wish to draw the attention of the authors to four points that they may wish to consider while preparing the final version of their manuscript:

1) Lines 13-16; Page 626 : The authors mention that measured OH reactivity reported by Sinha et al., 2008 was a factor of 4 higher than the calculated reactivity obtained using co-measurements of isoprene, its oxidation products and other VOCs. There is a minor error here in the quoted value. In fact the measured OH reactivity was a factor of 3 higher than the calculated OH reactivity due to the measured sinks such as isoprene, its oxidation products and other VOCs (Figure 11 in Sinha et al. 2008). The average value was 53 /s during the peak of diel emissions and the highest value was indeed as high as 73 /s, as rightly noted by Ingham et al.

2) It is commendable of the authors to have addressed the issue of the NO+ HO₂ recycling interference as this issue has not been addressed adequately in previous studies, especially for the LIF based OH reactivity instruments. Note however that in Lines 15-18; Page 628, the wording of the authors is potentially misleading as they contend that at ambient NO >~ 1ppbV, both the LIF based methods and the CRM method suffer from the same degree of interference. This is not correct. Based on the results of the NO sensitivity study reported in Sinha et al. (2008), the CRM method performs better than the LIF based methods. There are two main reasons for this: The first one is the dilution effect in the CRM reactor. Ambient air is typically diluted by factor of 1.7- 2.2 in the CRM reactor and in fact one can even increase this dilution ratio in high NO- high OH Reactivity regimes, which are typical of polluted urban atmospheres. This means that NO is effectively present at less than half of its ambient air value within the CRM reactor. In theory, LIF based instruments could also adopt this dilution

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approach to minimize the NO interference but I imagine that this would be difficult in practice because of the high ambient air sample flow rates they typically consume (e.g. $\sim 300,000$ mL/min in the presented LIF instrument as against 100-150 mL/min ambient air flow in the CRM). Perhaps the authors would like to comment on this? The second factor that mitigates the OH recycling due to the NO + HO₂ reaction within the CRM reactor, is that pyrrole peroxy radicals which are formed due to the reaction of pyrrole with OH, buffer the NO and thus de-optimize the NO + HO₂ reaction channel, as the NO is no longer available exclusively for reaction with HO₂. Results of this higher NO threshold for the CRM method have already been reported in Sinha et al., 2008 (please see abstract and Figure 8) and they clearly show that the suppression in measured OH reactivity is significantly lower (more than a factor of 2 lower) than that reported in the present study (Figure 3 of Ingham et al.; a suppression of ~ 4 /s at ~ 13 /s of OH reactivity when ambient NO = 3.74 ppbV). On a related note have the authors also tested their instrument for ambient air humidity effects? Note also, that for other potential OH recycling reactions (e.g. terpenes + ozone), because the OH field at which LIF instruments operate is two orders of magnitude lower ($\sim 10^8$ molec/ml) than the CRM OH field (10^{10} molec/ml), and the LIF based methods rely on measuring the decay of the OH radical directly, the relative interference would be potentially higher for the LIF based methods compared to the CRM method.

3) As the authors make a mention of current OH reactivity instruments, it is perhaps worth mentioning in the manuscript, that the LIF and CRM methods differ somewhat in their approach to quantifying the ambient air OH reactivity. The LIF based methods measure the OH decay rate directly within a flow tube and hence measure the lifetime of the OH radical directly. Taking the inverse of the measured lifetime gives the OH reactivity (or k' as reported in the current manuscript). On the other hand, the CRM method measures the OH reactivity of the ambient air directly in terms of a pyrrole signal and taking an inverse of the directly measured OH reactivity (R_{air}) gives the lifetime of the OH radical. In this sense both the LIF and the CRM methods offer a good complement in terms of how they approach the quantification of the OH sinks

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in the ambient air. It is also clear from the description of LIF reactors in the present manuscript and previous studies that for sample flow (this becomes important for smog chamber studies), flow tube size (> 1 m long), costs and portability, the CRM reactor (reactor size < 15 cm) has several distinct advantages over the LIF based instruments. In terms of detection limits however, the LIF based instruments (detection limit ~ 1 per second) continue to have an advantage over the CRM based technique (currently not better than 3.5 /s).

4) As this manuscript presents a new field instrument for OH reactivity measurements, it would be most helpful for readers if the authors could list the detection limit, typical time resolution of the measurements, overall uncertainty of a typical measurement and the dynamic range of their new instrument in the abstract. From Figure 2, it seems that at high ambient OH reactivity values (60 per second and higher?) the extremely rapid reaction time (plotted on X-axis) would affect the LIF signal acquisition (plotted on Y axis) as the decay occurs too rapidly.

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