**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results" *by* S. Lou et al.

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Response to Comments by Vinayak Sinha

Comment

The manuscript presents a valuable dataset of OH reactivity measurements from the PRD campaign in China with a very good summary of published work on atmospheric OH reactivity measurements. The work clearly demonstrates the unique value of direct OH reactivity measurements for atmospheric chemistry and emission studies and I enjoyed reading this paper. I also look forward to the detailed technical paper on the OH reactivity instrument used by the authors, which unfortunately is still in press. Herein, I

would like to comment on what the authors have stated (please see below) regarding the possibility of the NO + HO_2 reaction (Reaction R9 in the discussion paper) recycling OH and causing an interference during OH reactivity measurements.

Statement (Pages 17043-17044 of the Discussion Paper: Line 22 onwards on Page 17043): "Recycling of HO_2 to OH (Reaction R9) can slow down the observed OH decay in the reactor, if the reaction rate of HO_2 and NO approaches the OH decay rate (Kovacs et al., 2003). This is generally the case after most OH has initially reacted with CO and VOCs, provided that sufficient NO is available. As a result, the observed kOH becomes systematically smaller than the true kOH. The data correction for the NO dependent effect can be large in measurement systems that inject not only OH into the reactor, but also HO_2. This is the case in instruments that generate OH and HO_2 as co-products by 185nm photolysis of water vapor (Kovacs et al., 2003; Shirley et al., 2006; Sinha et al., 2008; Ingham et al., 2009). For example, a correction factor of 1.4 at 5 ppb NO has been reported by Kovacs et al. (2003)." "The LP-LIF technique is much less affected by NO since no significant HO_2 is initially generated (Sadanaga et al., 2004b). Thus, in the present work, the error caused by reaction R9 is mostly negligible, reaching at most 5% at 5 ppb NO at PRD conditions. At higher NO, biexponential behaviour of the OH decays became noticeable, which can be explained by radical recycling. In this case, a biexponential fit was applied to the measured OH decay curves. The faster of the two fitted decay rate coefficients was used as an estimator of the true kOH. The validity of this approximation was confirmed by numerical simulations and laboratory experiments, demonstrating that the error of this approach is less than 10% for PRD conditions (Lou et al., 2009)."

Comment: The text in the above statement gives the impression that the CRM instrument described in Sinha et al. 2008 also has a correction factor due to the recycled OH by the NO + HO_2 reaction channel of the order of 1.4 as reported for the other LIF based OH reactivity instruments (works cited along with Sinha et al., 2008 in the statement), during ambient air OH reactivity measurements. However, such a statement

is inaccurate with regard to the CRM OH reactivity instrument for two main reasons: 1) The first reason is the dilution effect in the CRM reactor. Ambient air is typically diluted by a 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 inside the reactor. Thus, for ambient air NO mixing ratios of 5 ppb, the NO mixing ratio inside the CRM reactor is only circa 2 ppb. As can be clearly seen in Figure 8 of Sinha et al., 2008, at such NO mixing ratios (5 ppb ambient air; 2 ppb in CRM reactor) the measured OH reactivity tends to be under estimated by around 5%, and not a factor that is on the order of 1.4. In fact the 5% effect is more on the order of the correction factor also reported for the instrument used by the authors in their current work. In theory LIF based instruments could also use the dilution approach but their high sample flow rates (20 L/min for the instrument used in the present work as against 180- 220 ml/min in the CRM instrument) probably preclude such a possibility during extended measurement campaigns. 2) A second factor that mitigates the OH recycling due to the NO+ HO_2 reaction within the CRM reactor, is that pyrrole peroxy radicals which are formed due to the reaction of pyrrole with OH in the presence of O_2, buffer some of the NO and thus de-optimize the NO + HO_2 reaction channel, as the NO is no longer available exclusively for reaction with HO_2.

While the statement of Lou et al., 2009 that their instrument has less interference due to NO does apply to other LIF based OH reactivity instruments, the same does not hold true for the CRM OH reactivity instrument described in Sinha et al., 2008 . Therefore the authors should revise the text appropriately to avoid giving an erroneous impression.

Response

We agree and have removed the reference to Sinha et al. (2008) in our statement.

Comment

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It would also be helpful for readers if the authors could provide details on how much OH is typically produced in their reactor and what sort of HO_2/ OH ratio prevails at higher reactivity (say, at greater than $40s^{-1}$) within their flow reactor. Does the interference due to recycled OH from the NO+HO_2 reaction become higher under high NO and high OH reactivity regimes (note also from Fig 1 that the decay is already quite fast at $54s^{-1}$), as would seem to be the case in their system? What is the dynamic range of their instrument? Also did the authors use some filtering to remove data collected when NO was higher than a certain threshold in ambient air? From Table 2, I gather that NO values were as high as 30 ppb during the study.

Response

The photolytically generated initial OH concentration was less than 5×10^9 molecules per cm^3 during the field campaign (see answer to question 5 by referee #1). There is some lasergenerated HO_2 concentration in our instrument, which is less than 4×10^6 molecules per cm^3 (see answer to question 7 by referee #2). Given an initial HO_2 to OH ratio in the order of 10^{-3} in our instrument, the interference from conversion of laser generated HO_2 to OH by atmospheric NO is negligible. The interference from HO_2 recycling by NO has been explained in the paper. It contributes at most 5% at 5 ppb NO at PRD conditions. At higher NO (up to 30 ppb), biexponential behaviour of the OH decays is taken into account by a biexponential fit, resulting in an error of less than 10% (see experimental section 3.1). The lower end of the useful dynamic range is given by the limit of detection, which is determined by the variability of the zero decay measurements ($\sim 0.3s^{-1}$). To the high end, we have tested the instrument up to about $190s^{-1}$, which is much higher than the maximum values ($120s^{-1}$) observed in PRD. No data filter was applied with respect to ambient NO.