

## ***Interactive comment on “Comparison of OH concentration measurements by DOAS and LIF during SAPHIR chamber experiments at high OH reactivity and low NO concentration” by H. Fuchs et al.***

**H. Fuchs et al.**

h.fuchs@fz-juelich.de

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We thank the reviewer for his/her comments. Here are our responses to the specific comments:

**Comment:** I find it difficult to understand how the concentration of NO is determined. In Fuchs, 2010, I understand that NO was measured by chemiluminescence. Here (at least in the low NO regime) it is suggested that NO is determined by photostationary

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state calculations using NO<sub>2</sub> and O<sub>3</sub>. Is this correct? If so, is the reaction of organic peroxy radicals not an important source of NO<sub>2</sub>? In either case, please provide a statement on the NO measurement and its uncertainty.

**Response:** The statement “NO concentrations were determined by the photostationary state between NO<sub>2</sub> and O<sub>3</sub> (Fig. 1)” on p2086 l14 is misleading and will be deleted. NO and NO<sub>2</sub> concentrations were measured by chemiluminescence with a calibration uncertainty of 5%. For clarity, we will change l27-28 (p2085) to: “Measurements included NO and NO<sub>2</sub> (both chemiluminescence), O<sub>3</sub> (chemiluminescence), ...”.

**Comment:** Related to 1 (above). In the low NO regime, if [NO] is ≈150 ppt and [HO<sub>2</sub>] is ≈20 ppt, than only ≈2 % of the organic peroxy radicals are reacting with HO<sub>2</sub>. This should be noted, as while it is similar (I believe) to PRD, it is a different environment than BEARPEX, where ≈40 % of the peroxy radicals are calculated to react with HO<sub>2</sub> (e.g. [NO]≈65 ppt; [HO<sub>2</sub>]≈20 ppt).

**Response:** Assuming 150 pptv NO and 20 pptv HO<sub>2</sub> and taking ISOPBO<sub>2</sub> as a typical example for RO<sub>2</sub> species during these measurements, we calculate that approximately 25 % of the RO<sub>2</sub> radical reacts with HO<sub>2</sub> (taking reaction rate constants from MCM3.2 (295 K):  $k(\text{NO}+\text{ISOPBO}_2)=9.14 \times 10^{-12}$  and  $k(\text{HO}_2+\text{ISOPBO}_2)=2.38 \times 10^{-11}$ ). In fact, NO values during these measurements were as low as 60 pptv during part of the experiments (values in Table 2 are rounded maximum values), so that similar conditions as during the BEARPEX campaign were reached regarding the level of NO (but with different VOCs). We will extend Table 2 and give the range of NO mixing ratios during the oxidation part of the experiments. Moreover, the chemistry of RO<sub>2</sub> radicals at these low NO mixing ratios are currently under discussion and it is possible that H-atom migration with subsequent decomposition of the RO<sub>2</sub> radical may be even more important than the reaction with HO<sub>2</sub>.

**Comment:** Were any measurements made using chemical removal of OH to evaluate backgrounds in the LIF system? If so, please describe.

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**Response:** So far we did not perform tests using the chemical titration method, but this will be done in the future (see also our response to the first question by referee 1).

**Comment:** If the NO measurement is correct, the measurements described here do not rule out the possibility that interference from  $\text{HO}_2 + \text{RO}_2$  reaction products may produce LIF interferences in this (or other) instruments.

**Response:** The NO concentrations during our past field campaigns in China (Hofzumahaus et al. 2009, Lu et al. 2012a,b) and other isoprene-rich field sites (e.g., Schlosser et al. 2009) were generally within the range greater or equal 100 pptv. All we can say from comparisons between LIF and DOAS is that we have no hints for significant OH interferences in the LIF measurements within this range of NO mixing ratios. Potential interferences at even lower NO would need to be tested (see response to referee 1).

## References:

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Interactive comment on *Atmos. Meas. Tech. Discuss.*, 5, 2077, 2012.

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