

Author response to anonymous referee # 2 on “An intercomparison of HO₂ measurements by Fluorescence Assay by Gas Expansion and Cavity Ring-Down Spectroscopy within HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry)” by L. Onel et al.

Note: The changes in the manuscript addressing the comments of the referee #2 are highlighted in yellow below.

Q1. Page 7: Although Winiberg et al. demonstrated that the calibration factor derived from the self-reaction of HO₂ is independent of the water vapor concentration (when the rate constant for the HO₂+HO₂ reaction accounts for the water dependence of the reaction), the LIF-FAGE calibration factor is sensitive to the water vapor concentration due to quenching of the OH fluorescence. This should be clarified and the dependence of the calibration factor on the concentration of water should be explicitly given. Did the authors calibrate the FAGE instrument using the flow tube method under the water vapor conditions typically used in the HIRAC chamber?

The FAGE instrument was not calibrated using the flow tube method under the typical H₂O vapour concentrations within the chamber ($10^{13} - 10^{14}$ molecule cm³) as under such dry conditions the generated [HO₂] would be below the detection limit of FAGE ($\sim 8 \times 10^5$ molecule cm⁻³ for S/N = 2 and 2 min averaging time). As described in Sect. 2.3.1 of the main manuscript Winiberg et al. (2015) reported that the FAGE calibration factor for HO₂ (C_{HO_2}) obtained by the flow tube calibration using high water vapour concentrations is in good agreement with C_{HO_2} obtained by the kinetic method of calibration in relatively dry conditions in HIRAC. A similar result was obtained in this work: $C_{\text{HO}_2} = (2.6 \pm 0.4) \times 10^{-7}$ counts cm³ molecule⁻¹ s⁻¹ mW⁻¹ (flow tube calibration; ([H₂O] $\sim 7.5 \times 10^{16}$ molecule cm³) and $C_{\text{HO}_2} = (2.4 \pm 0.5) \times 10^{-7}$ counts cm³ molecule⁻¹ s⁻¹ mW⁻¹ (kinetic decay method; [H₂O] = $10^{13} - 10^{14}$ molecule cm³). Calculations using the collisional quenching rate coefficient of the OH excited state ($A^2\Sigma^+ (\nu' = 0)$) by H₂O, $k_{\text{Q(H}_2\text{O)}} = 6.91 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, (Bailey et al., 1999) and [H₂O] in the LIF detection cell during the calibration using the flow tube ($\sim 2.4 \times 10^{14}$ molecule cm⁻³) resulted in only $\sim 1\%$ lower fluorescence quantum yield relative to the value determined in the absence of H₂O. As Sect. 2.3.1 (the text below) mentions that Winiberg et al. (2015) found a relatively invariant C_{HO_2} between [H₂O] in the two calibration methods we think that no modification of the text is necessary.

“Winiberg et al. have shown that C_{HO_2} is relatively invariant between the high water vapour concentrations of the flow tube calibration method ([H₂O] $\sim 7 \times 10^{16}$ molecule cm⁻³) and the

relatively dry conditions in HIRAC ($[\text{H}_2\text{O}] \sim 10^{13} - 10^{14} \text{ molecule cm}^{-3}$) for the HO_2 recombination method.”

Q2. Page 9: Why were the FAGE measurements across the diameter of the HIRAC chamber done using different HO_2 radical sources compared to the Cl_2 radical source used for the main experiments?

In order to investigate into any $[\text{HO}_2]$ gradient across the HIRAC radius, HO_2 in steady-state was generated (for as long as possible). The photolytic mixtures used in the FAGE measurements across the chamber width have been chosen to generate a constant concentration of HO_2 over longer times than the photolysis of the $\text{Cl}_2/\text{CH}_3\text{OH}/\text{O}_2$ mixtures. The latter yield higher concentrations, but these start to change soon after photolysis has begun. Therefore, we think that no modification of the text is necessary.

Q3. Pages 18-19: The authors should clarify the method used to generate the linear fits shown in Figures 8 and 9. Are they unweighted linear regressions, or a bivariate weighted fit that takes into account the corresponding uncertainties associated with each measurement?

The linear fits shown in Figure 8b and 9b represent unweighted linear regressions.

Now the captures of the Figures 8b and 9b clarify the method used:

“Figure 8b ... Linear **unweighted** fits of the data generated gradients ...”