

The dependency on water vapour only becomes significant at higher water number concentrations for NO 45 ppm at 300 mbar as shown in figure 14. New measurements at 10 and 30 ppmv NO at 300 mbar show a clear dependency with [H₂O] which has to be taken into account in the analysis of ambient air measurements at these operating conditions. The water vapour dependence of eCL decreases significantly from 10 ppm to 45 ppm. For water vapour concentrations in the range of 4 -14 x 10¹⁶ molecule cm⁻³ of relevance for HALO flights, this results in the water vapour impact on the eCL being negligible. This is shown more explicitly in the new figure 14 in the manuscript.

As described in Hastie et al., (1991) and Reichert et al., (2003), the chain length (CL) of a PERCA reactor can be expressed using a resistance model as follows:

$$\frac{1}{CL} = \left(\frac{1}{CL_{HO_2}} + \frac{1}{CL_{OH}} \right)$$

$$\frac{1}{CL} \approx \frac{1}{P_{NO_2}} \cdot \left(\frac{\sum HO_2 \text{ removal rates}}{\sum HO_2 \text{ propagating rates}} + \frac{\sum OH \text{ removal rates}}{\sum OH \text{ propagating rates}} \right)$$

And if only the predominant processes are considered, as:

$$\frac{1}{CL} \approx \frac{1}{P_{NO_2}} \cdot \left(\frac{k_{wHO_2} \cdot k_{HNO_3}[NO][M]}{k_{NO+HO_2}} + \frac{k_{wOH} \cdot k_{HONO} \cdot [NO]}{k_{CO+OH} \cdot [CO]} \right)$$

P_{NO_2} is the probability of radical conversion into NO₂, k_{wHO_2} and k_{wOH} are the wall losses of HO₂ and OH respectively, k_{NO+HO_2} is the rate constant for NO₂ production from HO₂ + NO reaction, k_{HONO} is the rate constant for HONO formation from OH + NO reaction, k_{CO+OH} is the rate constant for HO₂ formation from OH + CO reaction. In the presence of H₂O, HO₂ water clusters are formed as postulated by Reichert et al., (2003).

Our interpretation of these novel results is that as the NO is increased from mixing ratios of 10 to 45 ppm at 300 mbar, the CL_{OH} is reduced, because the rate of the chain termination termolecular reaction of OH with NO making HONO increases, and the CL_{HO_2} is increased, because the rate of the propagation reaction between NO and HO₂ increases. As a result the CL begins to be dominated by the CL_{OH} , which is independent of water vapour.

The new series of measurements are now included in Figure 14 and the text has been extended for clarification (Lines 359-371):

“In [this work](#) radical mixtures were sampled at 25 °C for relative humidity between 2 % and 25 %. This leads to a ca. 20 times increase in the absolute [H₂O]. These conditions cover the [H₂O] expected for a larger T range (-20 – 30 °C) during airborne measurements in the free troposphere at 200 and 300 mbar inlet pressures. [Figure 13](#) shows the [H₂O] in the air probed versus the [H₂O] in the inlet for real measurements on board of the HALO aircraft. The results in [figure 14](#) for 45 ppm NO ([NO] 3.28 x 10¹⁴ molecules cm⁻³ at 300 mbar) indicate that variations in the sample humidity do not lead to additional uncertainty in the RO₂* retrieval as the PeRCEAS

eCL remains invariable within the experimental error up to $[H_2O] \sim 1.4 \times 10^{17}$ molecules cm^{-3} . In contrast, for 10 ppm and 30 ppm NO in the reactor ($[NO] 7.29 \times 10^{13}$ and 2.19×10^{14} molecules cm^{-3} at 300 mbar) the eCL shows a clear dependency with the ambient $[HO_2]$. The comparison with the eCL values obtained by Reichert et al (2003) at 1 atmosphere indicate a eCL dependency on $[H_2O]$, temperature and pressure having a different pattern for 45 ppm NO in the reactor. This is explained by invoking the competition in the amplification chain length, CL, between HO_2 and OH removal rates, as explained in Hastie et al., (1991) and Reichert et al., (2003). At $[NO] \sim 3.28 \times 10^{14}$ molecules cm^{-3} the CL begins to be dominated by the rate of the termination termolecular reaction of OH with NO, which is independent of water vapour. This eCL dependency has to be taken considered in the analysis of ambient air RO_2^* measurements.”