

## 1. Introduction

- Concentrations of HO<sub>2</sub> and RO<sub>2</sub>, critical radicals in many atmospheric processes, are often **overestimated** in **atmospheric models**.<sup>1</sup> These discrepancies have sometimes been attributed to the **heterogeneous loss** onto **atmospheric aerosols**. There is a significant lack of data for the uptake of HO<sub>2</sub> or RO<sub>2</sub> onto organic aerosols, even though they represent a high proportion of atmospheric aerosols.
- The principal objective of this project is to explore the heterogeneous reactions of HO<sub>2</sub> and RO<sub>2</sub> occurring on the surface of atmospherically relevant secondary organic aerosols.

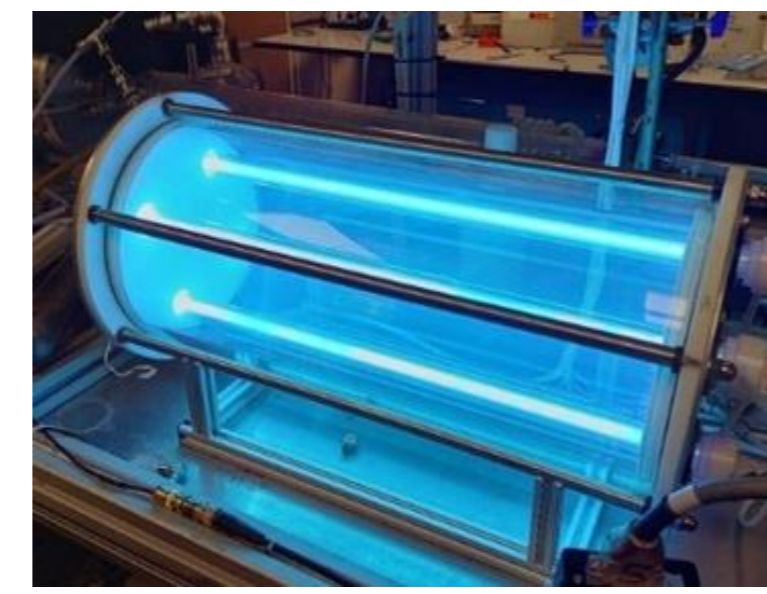


Figure 1: Picture of the PAM chamber at Leeds

## 2. SOA Formation

- SOAs were formed in a Potential Aerosol Mass (PAM) Chamber from precursor VOCs, **α-pinene**, **Δ-limonene** and **1, 3, 5 – trimethylbenzene (TMB)**.
- The PAM chamber is designed to make the maximum amount of aerosols from the precursor VOC by using a high concentration of oxidant (O<sub>3</sub> or OH).
- A **Scanning Mobility Particle Sizer (SMPS)** characterised the physical properties of the SOA produced.

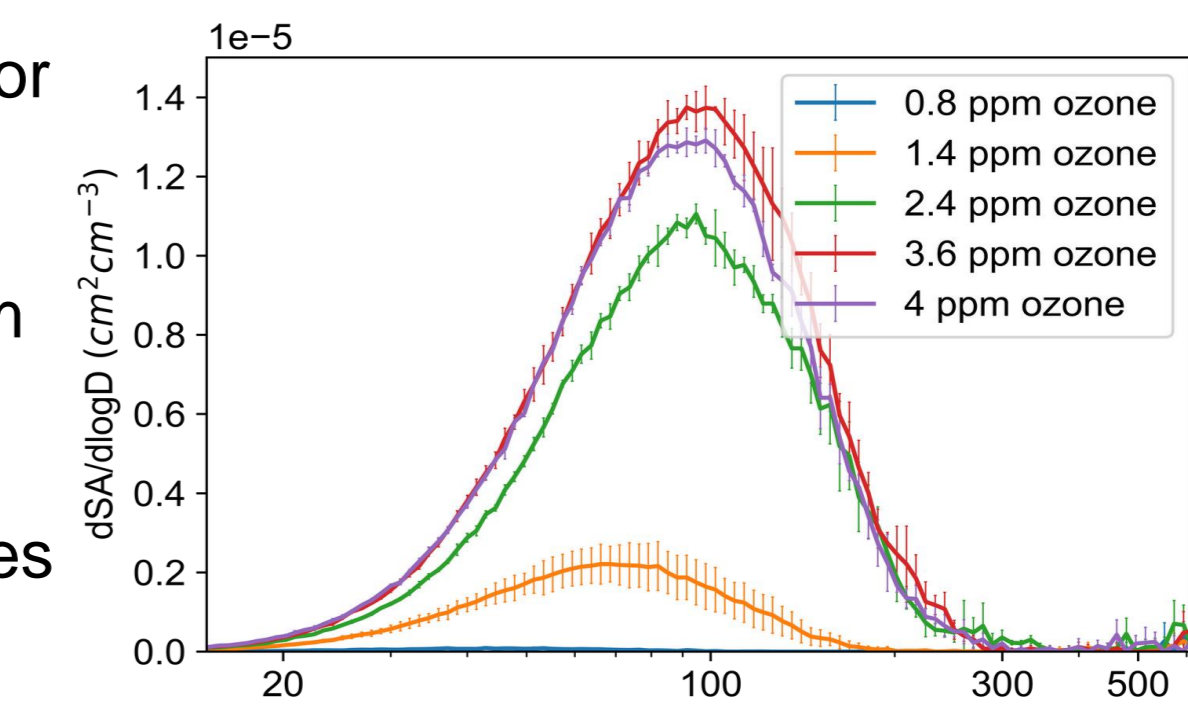


Figure 2: Aerosol surface area size distribution of SOA produced from the ozonolysis of 1 ppm α-pinene with different concentrations of ozone

## 3. Measuring HO<sub>2</sub> uptake onto SOA

- A flowtube coupled to a **FAGE (Fluorescence Assay by Gas Expansion)** was utilised to measure the uptake coefficient of HO<sub>2</sub> onto SOA.
- HO<sub>2</sub> is injected through a moving injector. The moving injector allows the exposure time of HO<sub>2</sub> and the aerosols to be changed within the flowtube, and a decay in the HO<sub>2</sub> concentration can be measured as a function of the exposure time (Figure 4).

HO<sub>2</sub> is first converted into OH by reaction with NO, and then OH is detected by on-resonance laser-induced fluorescence (LIF) in the FAGE cell.

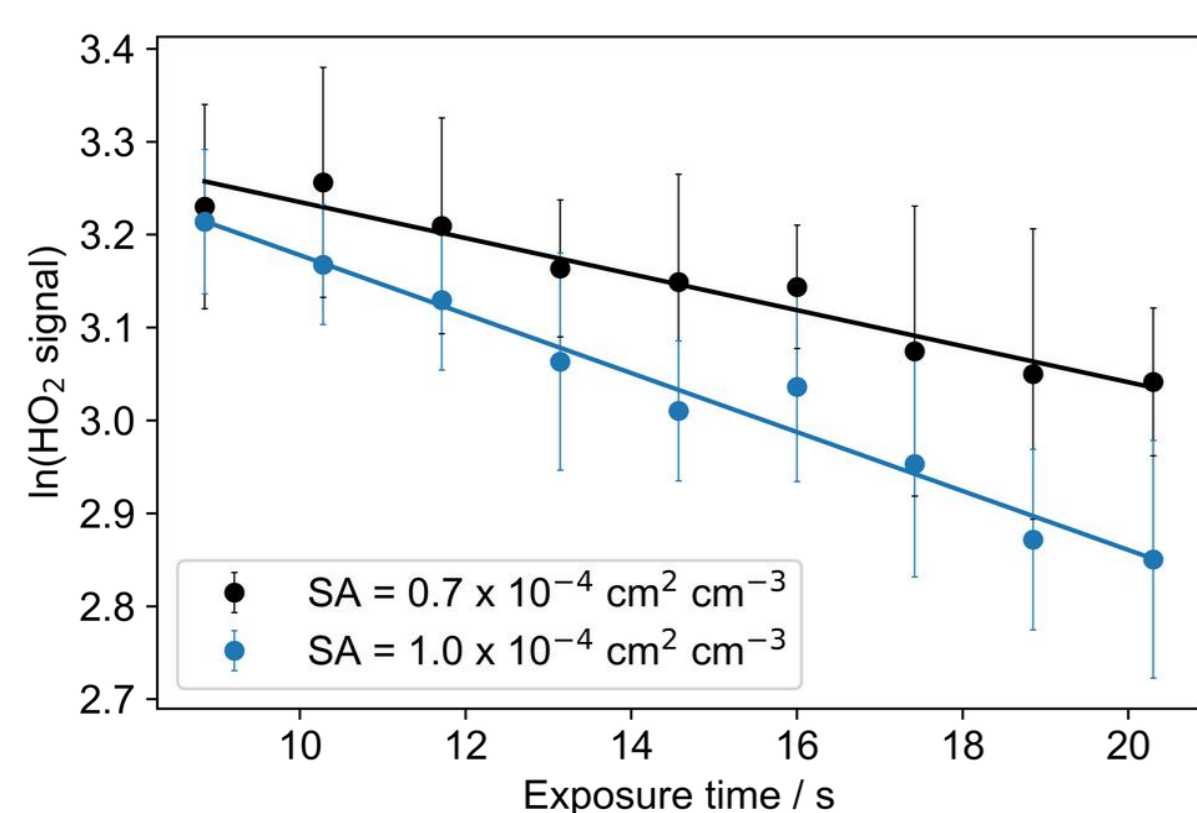
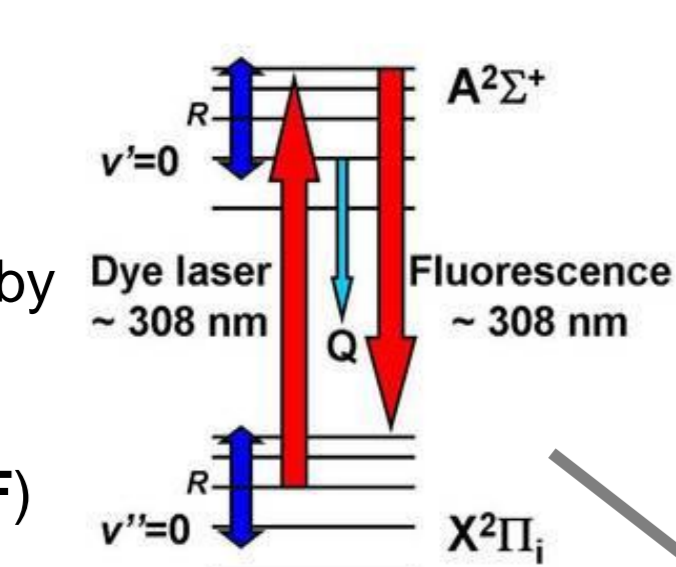


Figure 4: The ln(HO<sub>2</sub> signal) decay with the exposure time inside the flowtube with 1,3,5- trimethylbenzene (TMB) SOA with total surface area 0.7 (black) and 1.0 (blue) × 10<sup>-4</sup> cm<sup>2</sup> cm<sup>-3</sup> showing, with pseudo-first-order rate coefficient (k<sub>obs</sub>) 0.018 ± 0.002 (black) and 0.035 ± 0.003 (blue) s<sup>-1</sup>. Measured at 298 K and relative humidity (RH) of 36%.

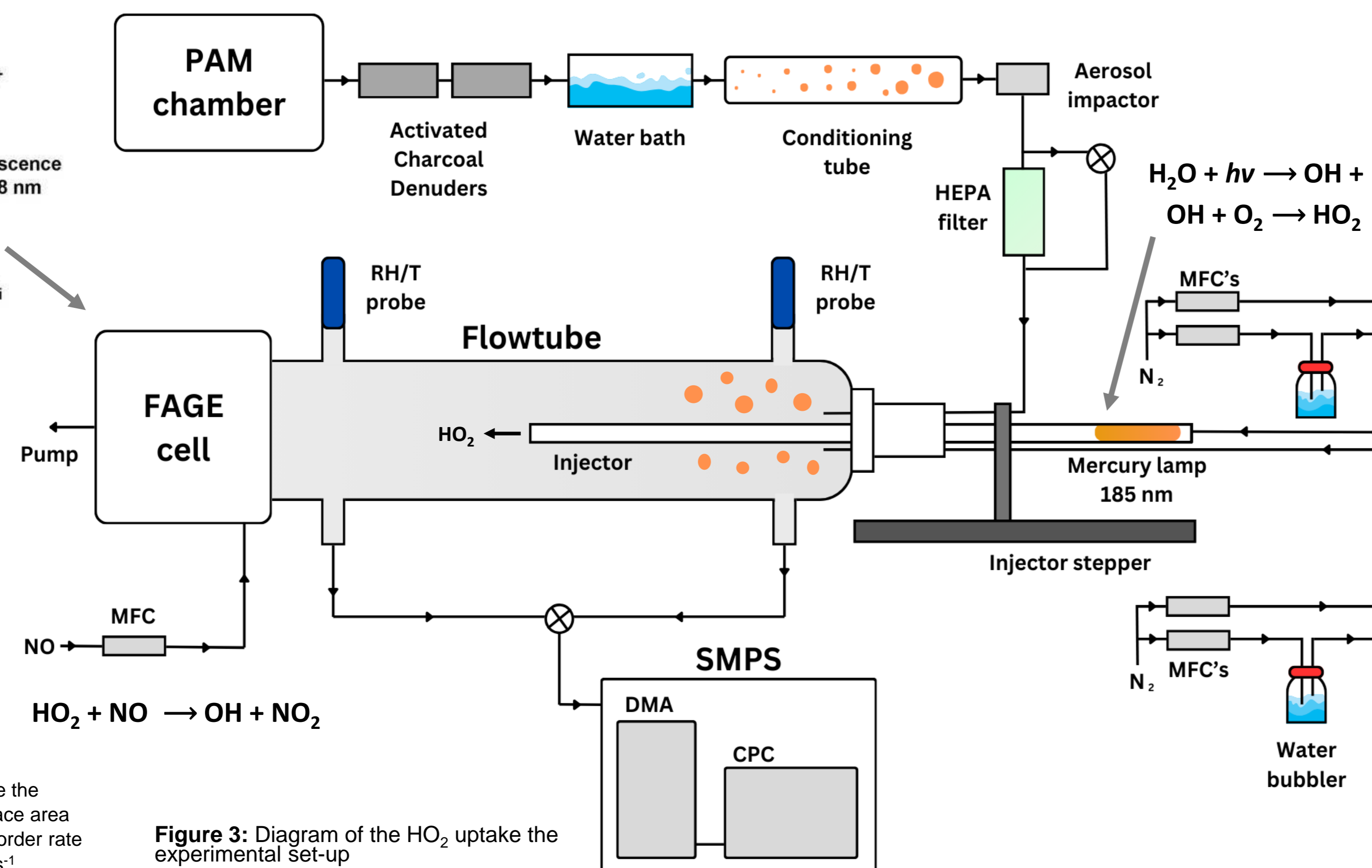


Figure 3: Diagram of the HO<sub>2</sub> uptake the experimental set-up

- The decay in HO<sub>2</sub> signal is measured at different aerosol concentrations to produce a graph of the pseudo first-order rate coefficient (k') pseudo first-order against total aerosol surface area (SA) (Figure 5). The uptake coefficient, γ<sub>obs</sub> can then be calculated from k'.
- Where ω<sub>HO<sub>2</sub></sub> is the molecular thermal speed of HO<sub>2</sub> and S is the total aerosol surface area.

$$k' = \frac{\gamma_{obs} \omega_{\text{HO}_2} S}{4}$$

- The uptake coefficient, γ(HO<sub>2</sub>), for TMB SOA was measured to be 0.002 ± 0.003. This is similar to the previous measurements by Lakey et al. (2016) of 0.004 ± 0.002.<sup>2</sup> Limonene SOA formed from O<sub>3</sub> oxidation yielded a low uptake coefficient, γ(HO<sub>2</sub>) < 0.001.

Similar low uptake coefficients have also been measured for α-pinene SOA.<sup>2</sup>

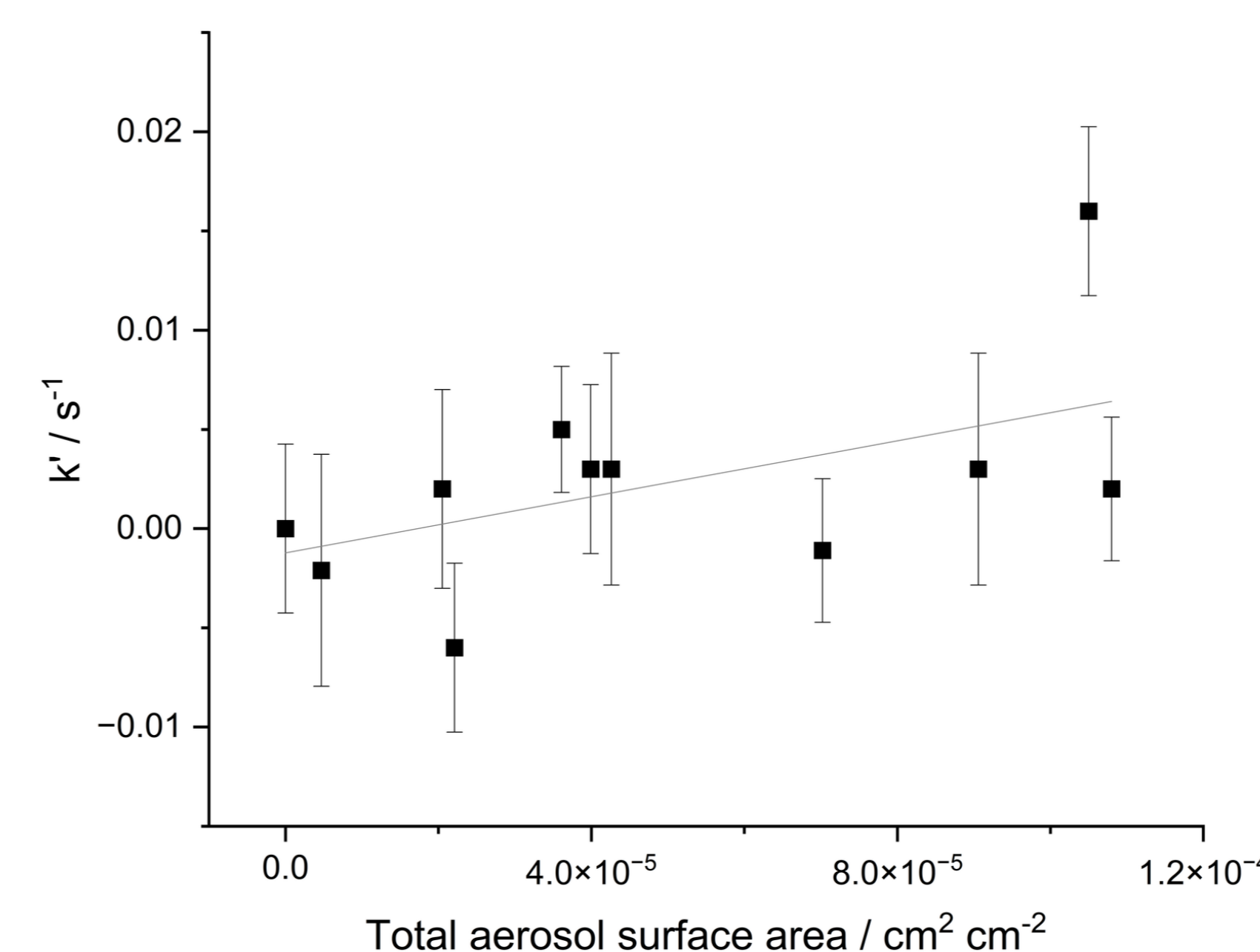


Figure 5: The pseudo-first-order rate coefficient for the uptake of HO<sub>2</sub>, γ(HO<sub>2</sub>), onto TMB SOA as a function of total aerosol surface area. The uptake coefficient calculated from the gradient of these graphs is 0.003 ± 0.002. Measured at 298 K and relative humidity (RH) of 36%. Error bars represent one standard deviation.

- These uptake coefficients were measured at a range of relative humidities (Table 1), as it has been shown previously for sucrose aerosols that uptake could increase as the viscosity of an aerosol decreases with higher relative humidity.<sup>2</sup>

RH (%)	VOC precursor	Uptake
36	TMB	0.003 ± 0.002
75	TMB	0.001 ± 0.003
80	TMB	0.002 ± 0.002
36	Limonene	<0.001
53	Limonene	<0.001
67	Limonene	<0.001

Table 1: The pseudo-first-order rate coefficient for the uptake of HO<sub>2</sub>, γ(HO<sub>2</sub>), onto TMB and Limonene SOA measured at different relative humidity.

## 4. RO<sub>2</sub>/HO<sub>2</sub> Radicals Observed in the Presence of SOA

- An interference signal was measured when only SOAs were present in the flowtube and NO was on in the FAGE cell. This interference could be due to HO<sub>2</sub> or RO<sub>2</sub> species converted to OH in the FAGE cell.
- This interference signal increased as the aerosol surface area for limonene SOA increased. This interference is absent when the SOA enters the FAGE cell directly from the PAM chamber (Figure 7). It is a gas-phase species that forms only when the aerosol flows through the flow tube.

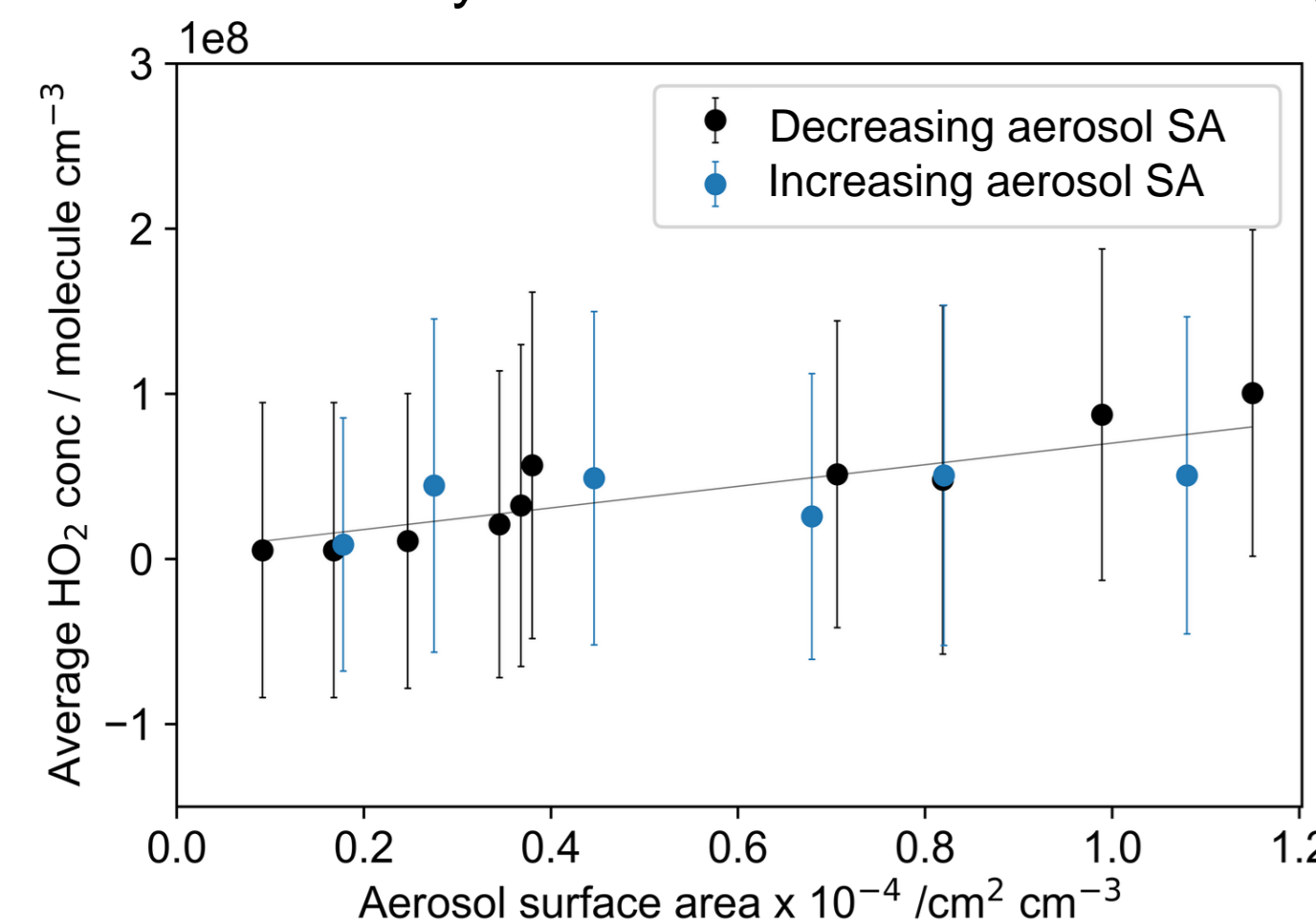


Figure 6: The interference signal converted to average HO<sub>2</sub> concentration that was measured when only Limonene SOA was present in the flowtube and NO to the FAGE cell was on at different aerosol surface areas.

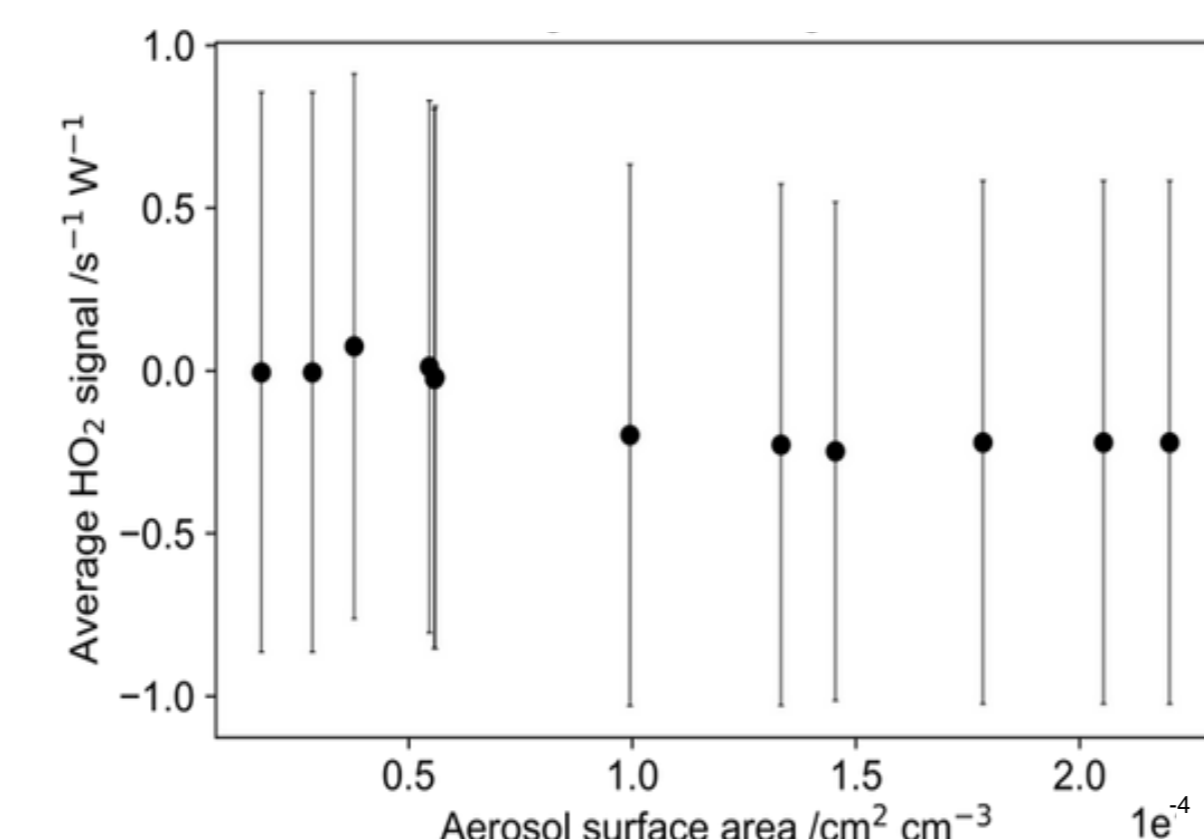


Figure 7: The interference signal measured when limonene SOA enters the FAGE cell directly after the PAM chamber (and doesn't enter the flowtube) at different total aerosol concentrations.

- RO<sub>2</sub> and HO<sub>2</sub> display different dependencies with NO concentration due to RO<sub>2</sub> needing to react with two NO molecules before OH is generated and detected by LIF.<sup>3</sup> The NO dependence of the interference is less steep than the dependence for HO<sub>2</sub>, providing some evidence that the interference could be due, at least in part, to an RO<sub>2</sub> species.

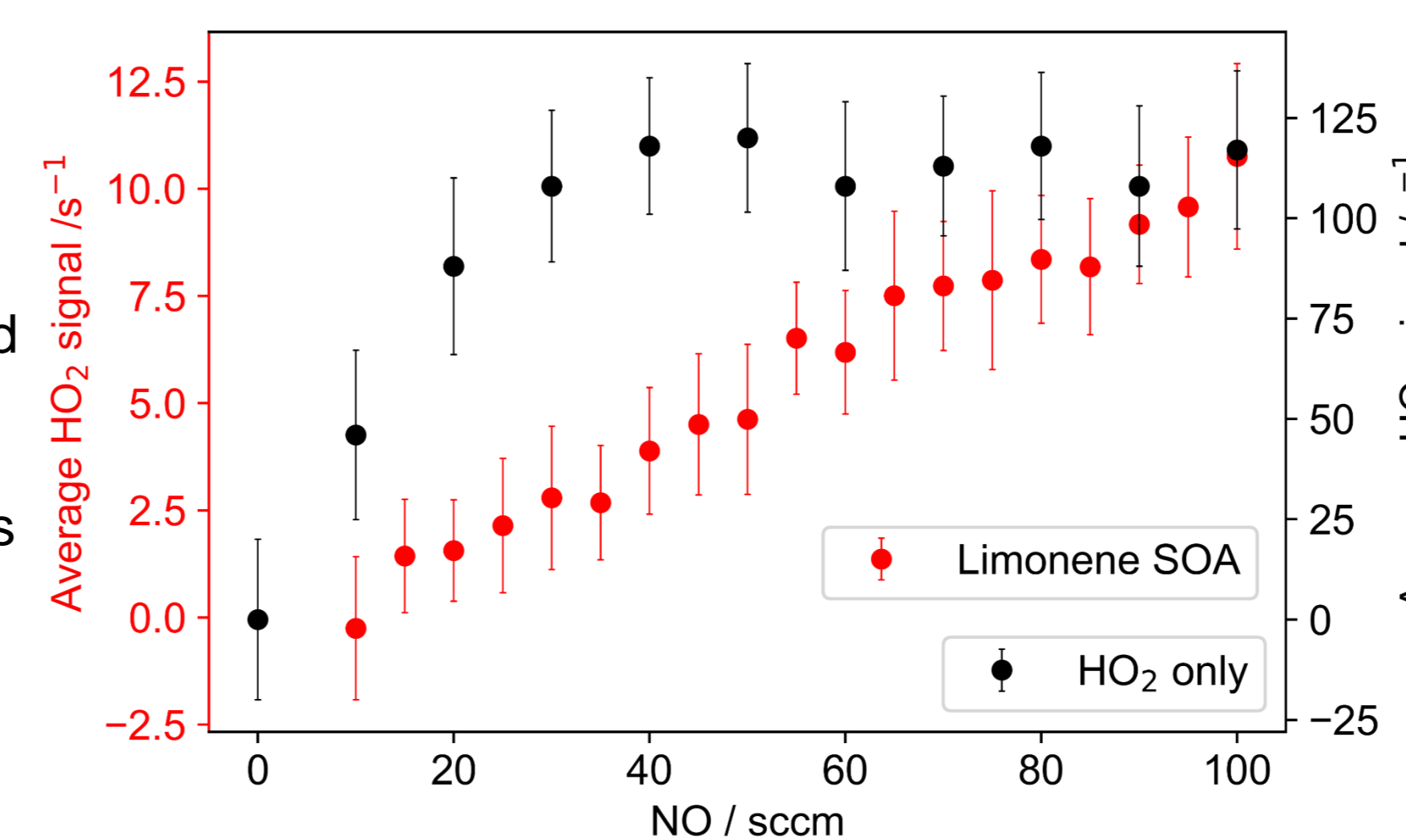


Figure 8: NO dependence (10% NO in N<sub>2</sub>) of the FAGE signal when only Limonene SOA is in the flowtube (red) and during a HO<sub>2</sub> calibration.

## 5. Conclusions

- Experiments so far have shown a relatively low and sometimes undetectable uptake of HO<sub>2</sub> onto signal component SOAs (TMB, Limonene & α-pinene) with no observable relationship between uptake and relative humidity. Future studies will look at the HO<sub>2</sub> uptake onto more atmospherically relevant SOAs.
- Future work will also emphasise identifying and quantifying the species causing the interference when only SOA is present.

## References

- Whalley et al., ACP, 2018
- Lakey et al., ACP, 2016
- Whalley et al., AMT, 2013

