Implementation of a chemical background method (OH-CHEM) for measurements of OH using the Leeds FAGE instrument: Characterisation and observations from a coastal location

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1. Introduction

- The hydroxyl radical (OH) is the most important day time oxidant, and controls the removal of pollutants and the formation of O_3 in the troposphere. It is therefore crucial that the atmospheric chemistry of OH is well understood.

- Chemical box models serve as a vital tool to assess our understanding of tropospheric oxidation chemistry, and the short lifetime of OH makes it an ideal candidate for simulation. However, recent comparisons of modelled [OH] to those observed in low-NO_x environments with significant biogenic VOC loadings show consistent, and often severe (up to tenfold) underpredictions (Lelieveld et al., 2008; Whalley et al. 2011; Lu et al., 2012; Mao et al., 2012), suggesting missing sources of OH.

- Recent studies (Mao et al., 2012; Novelli et al., 2014) have suggested that some fluorescence assay by gas expansion (FAGE) instruments, used to make most of the reported observations of OH in such environments, may suffer from positive biases in OH measurement. In these studies, implementation of an alternative method to determine the OH background signal, where OH is chemically removed prior to sampling (OH-CHEM), resulted in substantial reductions in measured [OH] (Mao et al., 2012; Novelli et al., 2014) and improved model agreement (Mao et al., 2012).

- As interferences are likely to be highly dependent on instrument design and operating conditions, other FAGE instruments should be tested on an individual basis, which includes some operation in the field using OH-CHEM. As such, the Leeds FAGE instrument was modified to incorporate a new inlet pre-injector (IPI) sampling system to allow measurements of OH-CHEM in order to assess the magnitude of any interference.

2. The Leeds Ground-Based FAGE Instrument

- Ambient OH is measured using laser-induced fluorescence (LIF). Briefly, ambient air is drawn through a 1.0 mm diameter pinhole at ~7 slm into a stainless steel cell held at ~1.5 Torr. An all solid-state laser system is used to excite OH via the $A^2\Sigma^+(v'=0)\leftarrow X^2\Pi(v''=0)$ electronic transition at 308 nm. The resultant fluorescence at 308 nm is detected by a micro-channel plate (MCP), and the signal analysed by gated photon counting. The background signal is normally obtained by scanning the laser wavelength off-resonance from the OH transition (OH-WAVE).

- Hydroperoxy (HO_2) and alkylperoxy (RO_2) radicals may be measured after conversion to OH by reaction with NO (Fuchs et al., 2008; Whalley et al., 2013).

- FAGE is not an absolute technique and therefore requires calibration. This is achieved by supplying known concentrations of OH via a turbulent flow tube held at ~45° to the instrument inlet, where OH and HO_2 are formed by the photolysis of water vapour at 184.9 nm in a flow of humidified zero air (40 slm). Chemical actinometry is used to measure the product of lamp flux and photolysis exposure time in order to calculate radical concentrations.

3. IPI Design

- The Leeds IPI (Fig. 1) is similar in concept to the design of Mao et al. (2012) and consists of a 4 cm length, 1.9 cm ID PFA cylinder embedded inside an aluminium housing, which seals to the FAGE cell via an O-ring base flange (as shown in Fig. 2A).

- The scavenger is injected into the centre of the PFA flow tube via four 0.25 mm ID needles at one of three possible injection heights, with optimum results at a distance of 40 mm from the instrument pinhole. The low bore capillary tubing increases the pressure inside the needles, facilitating mixing of the scavenger into the ambient air stream.

- In this work propane was used as the OH chemical scavenger, with similar results obtained for perfluoropropene (C_3F_6). The propane (0.45-9 sccm) was diluted in a flow of N_2 (500 sccm) prior to injection.

- In order to reduce radical wall losses, excess ambient air is drawn through the IPI to generate a sheath flow. This minimises the FAGE sampling of air from near the walls of the cylinder, housing and turret (Fig. 2).
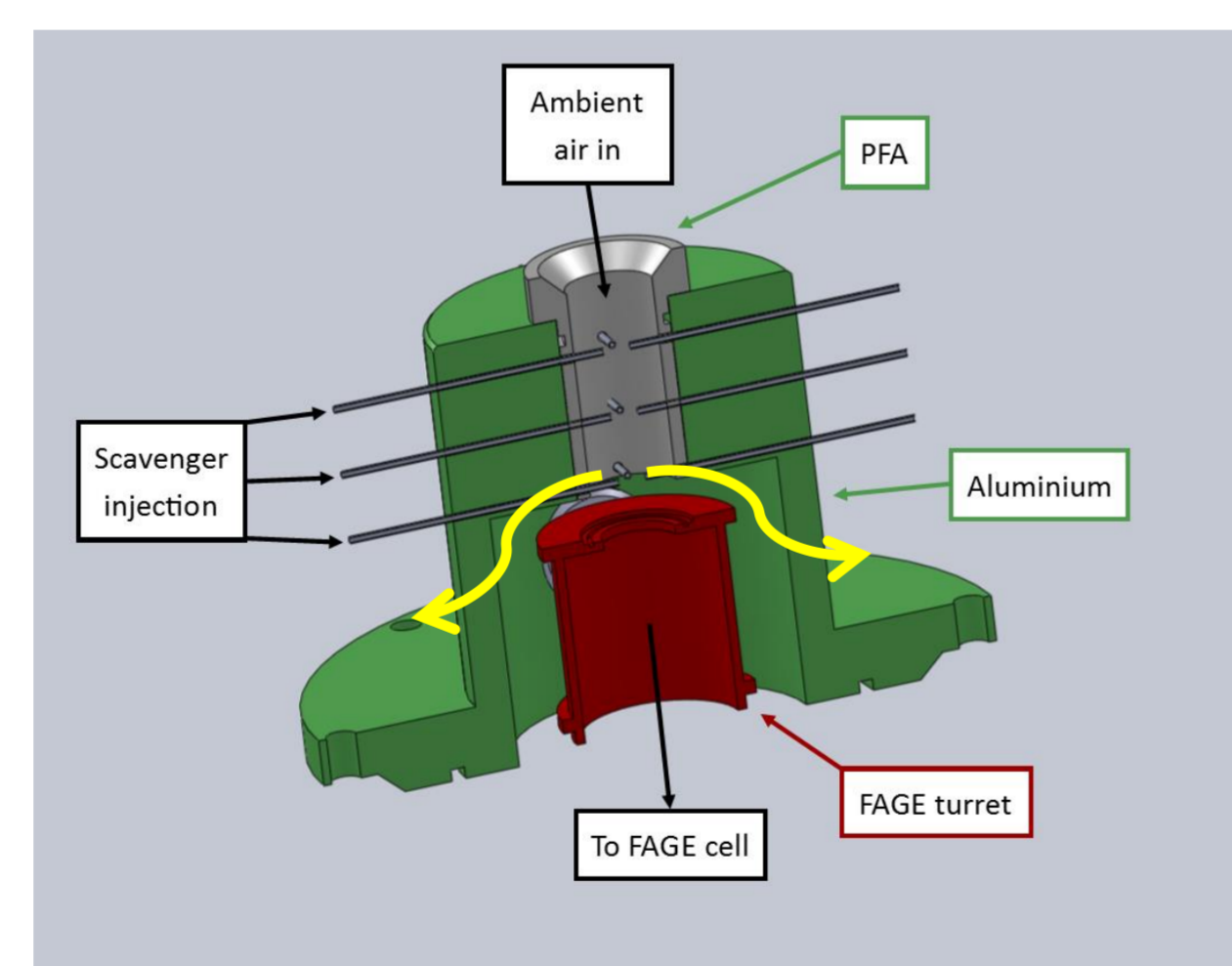

Figure 1. Labelled SolidWorks model of the Leeds IPI. The yellow arrows indicate the direction of the sheath flow (see text).

Figure 2 (right). Side (A) and top (B) view photographs of the IPI system, mounted on the HO_x fluorescence cell. A scroll pump pulls air through four ¾" holes located just above the base flange of the IPI to provide the sheath flow.

4. IPI Characterisation

- In order to minimise radical wall losses and maximise the OH removal efficiency the operating conditions of the IPI were varied. Experiments were performed by generating radicals in an analogous manner to calibrations, except with the flow tube held at ~90° to and ~3 cm above the PFA cylinder (to minimise perturbation to the flow profile inside the IPI).

- The ratios (IPI on:off) of the calibration factors at an optimum sheath flow of ~25 slm (τ ~24 ms) are shown in Table 1. Relative sensitivities were also determined through an ambient comparison in Leeds, in which simultaneous HO_x measurements were made using two adjacent cells. The presence of the IPI results in in a ~37-45% loss in OH sensitivity and only ~6-10% for HO_2, and the overall uncertainty in measurements of OH is estimated at ~20% (1σ).

- Figure 3 shows that an optimum scavenging efficiency (~99% OH removal) was found at a propane concentration of 2.7×10^{15} molecule cm^{-3} (110 ppmv). Repeat experiments showed that this loss was reproducible (99.29 ± 0.25%). However, the OH remaining is much larger than the theoretical, suggesting that the removal efficiency is limited by mixing.

- Internal OH loss, i.e. reaction of the scavenger with OH formed *inside* the cell, could lead to a positive bias in the measurement of ambient [OH]. This was investigated by monitoring changes in "HO_2" signal (with NO injection just below the pinhole), but no evidence for internal removal was found.

Table 1. Relative sensitivities (IPI on:off, ±1σ) for OH and HO_2 when sampling through the IPI.

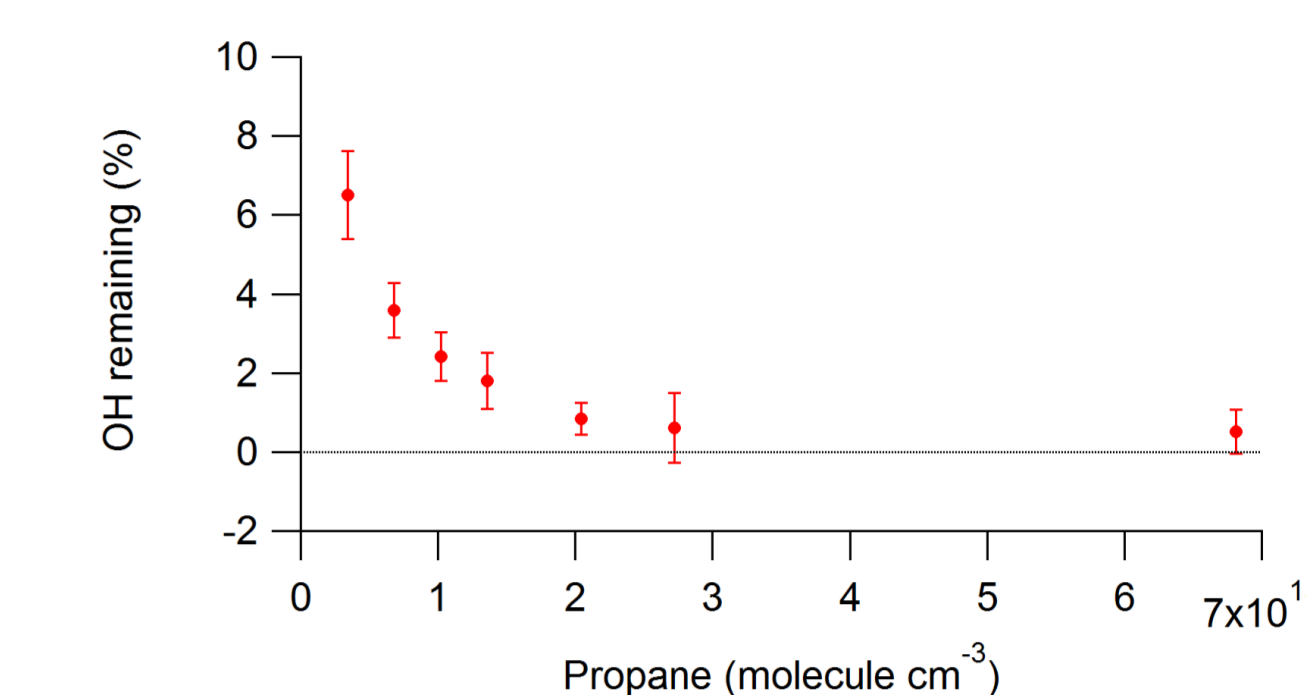|	OH	HO_2
Calibration	0.625 ± 0.076	0.90 ± 0.16
Ambient	0.550 ± 0.056	0.940 ± 0.092

Figure 3. OH remaining against propane concentration. Error bars correspond to 1σ variability of the OH signal.

5. Initial Observations from a UK Coastal Site

- The Leeds IPI was first deployed during the ICOZA (Integrated Chemistry of OZone in the Atmosphere) project, which took place at the Weybourne Atmospheric Observatory (WAO), Norfolk, UK, in July 2015. The site is impacted by a range of contrasting air masses, from clean Arctic air to processed emissions from the UK (e.g. London) and Northern Europe.

- Consecutive measurements of OH made using the two background methods (OH-WAVE and OH-CHEM) generally show very good agreement, mostly within 5×10^5 molecule cm^{-3} (Figs. 4-6). However, some discrepancies are observed for short periods of time (Fig. 4), the reasons for which are subject to ongoing investigation.
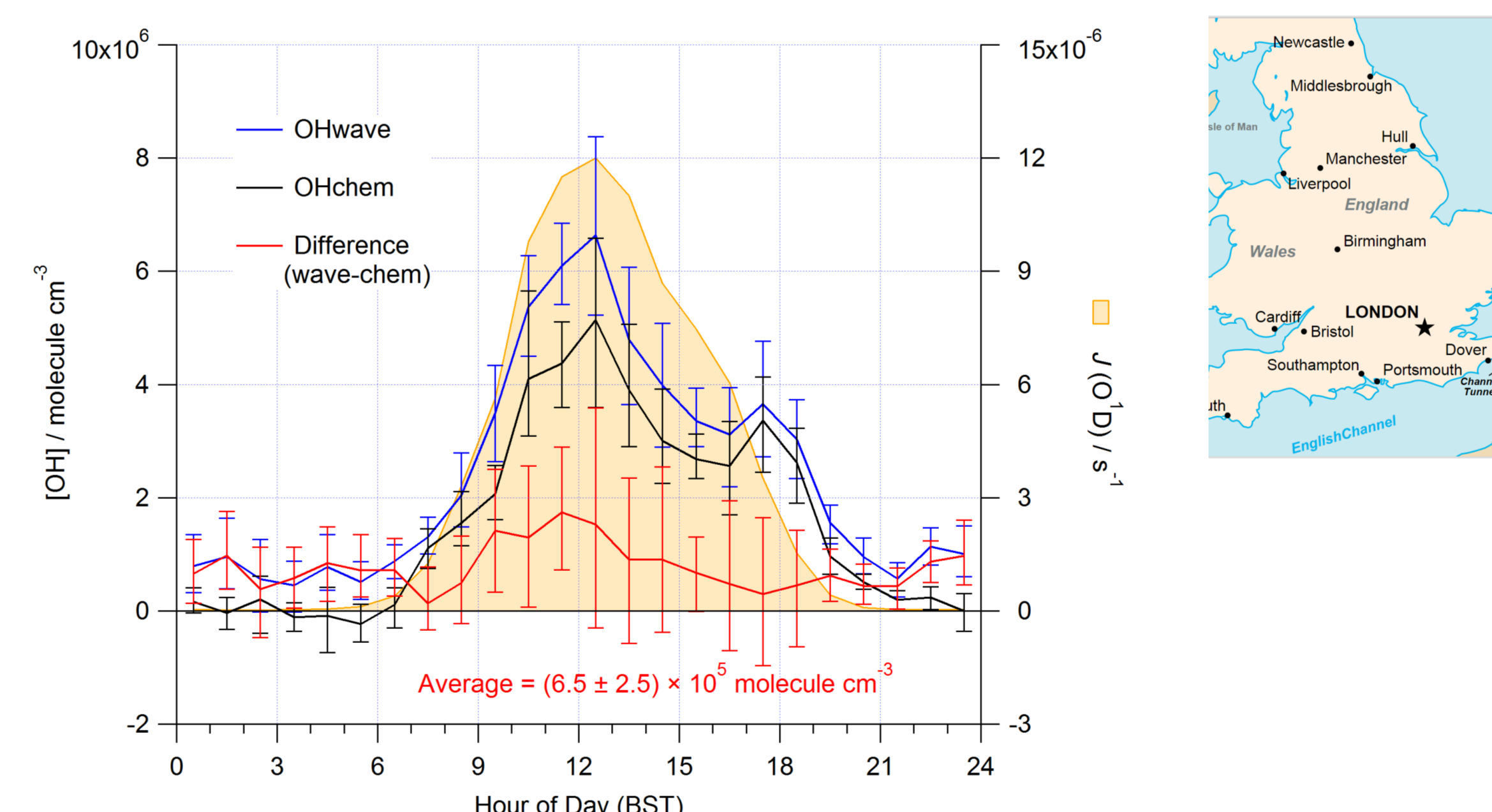

Figure 5. Diurnal profile of measured OH-WAVE (blue), OH-CHEM (black), their difference (red), and J (O^1D) (orange line and shaded area). Error bars correspond to the 95% confidence interval of the ambient variability within each time bin.

Average = (6.5 ± 2.5) × 10^5 molecule cm^{-3}
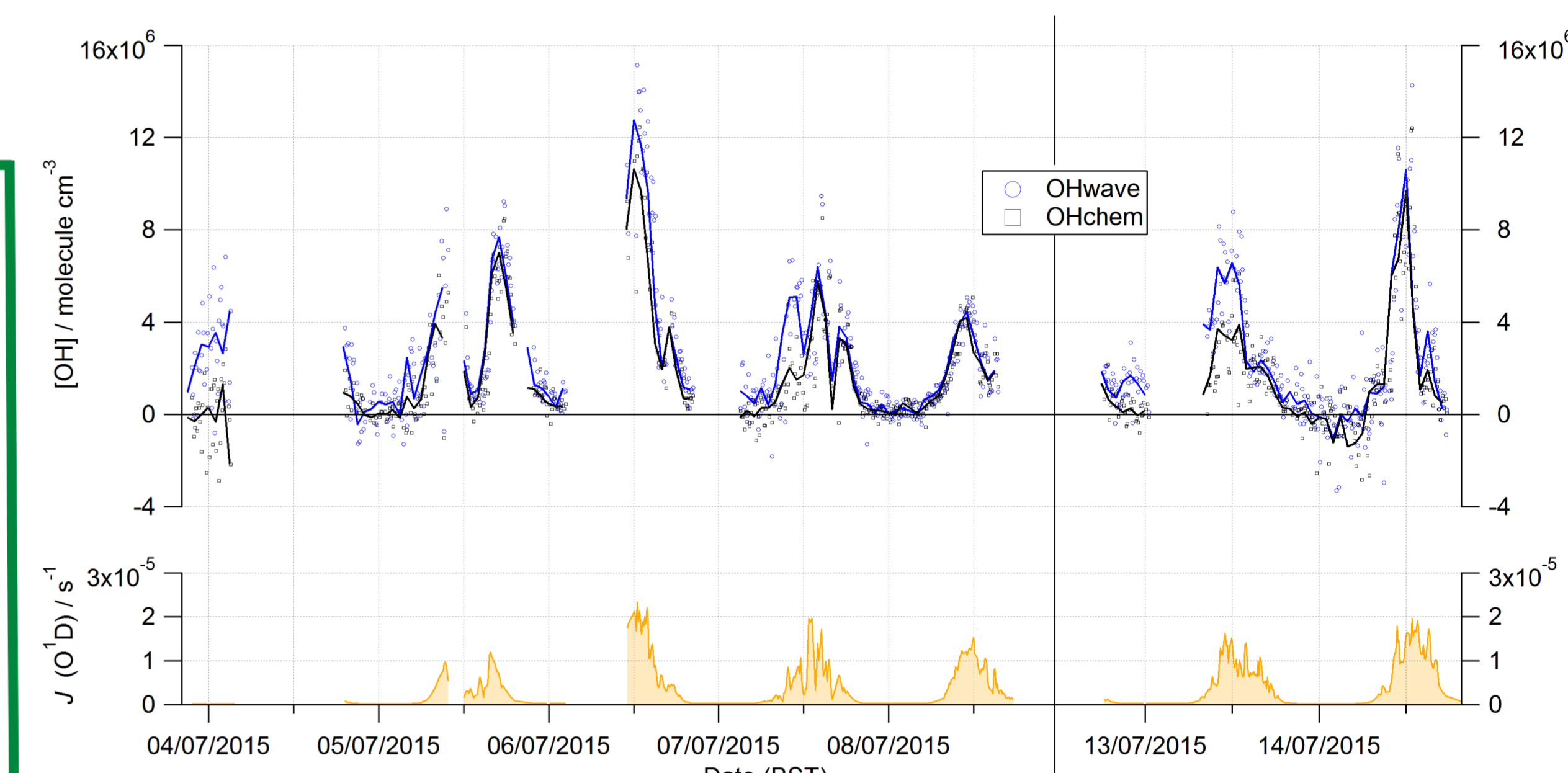

Figure 4. Time series of ambient data obtained between 3-8 and 12-14 July 2015. Top: FAGE measurements of OH-WAVE (blue circles) and OH-CHEM (black squares); solid lines correspond to hourly averages. Bottom: filter radiometer measurements of J (O^1D).
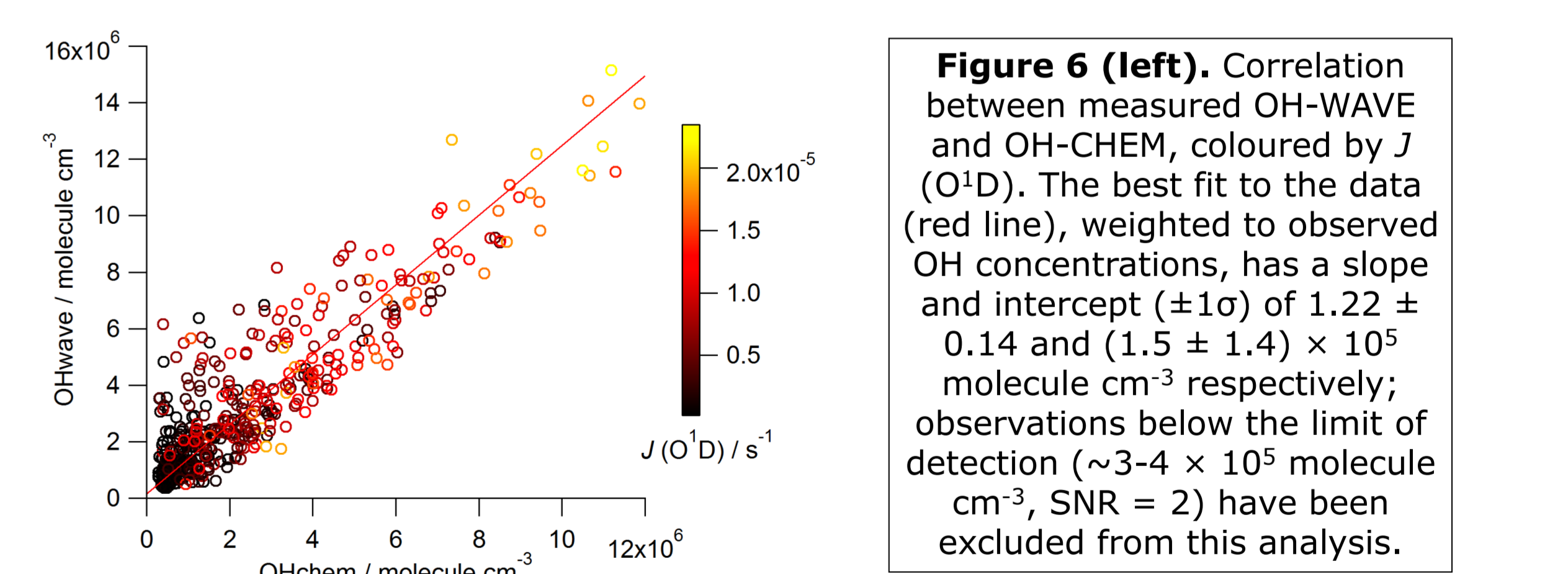

Figure 6 (left). Correlation between measured OH-WAVE and OH-CHEM, coloured by J (O^1D). The best fit to the data (red line), weighted to observed OH concentrations, has a slope and intercept (±1σ) of 1.22 ± 0.14 and (1.5 ± 1.4) × 10^5 molecule cm^{-3} respectively; observations below the limit of detection (~3-4 × 10^5 molecule cm^{-3}, SNR = 2) have been excluded from this analysis.

6. Conclusions

- The OH-CHEM method has been implemented in the Leeds ground-based FAGE instrument and characterised in terms of sensitivity and OH removal efficiency.
- Initial deployment of the IPI at a UK coastal site was successful, where good agreement between the two background methods (OH-WAVE and OH-CHEM) suggests a minimal interference in OH measurements, at least in this environment. Further analysis of periods of disagreement in this data set is necessary.
- Future field campaigns should seek to assess the extent of interferences in a range of environments, including low-NO_x, biogenic regions where model-measurement discrepancies have up to now been the largest, and also in urban environments containing a wide range of VOCs.

7. References

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8. Acknowledgements