



Implementation of a chemical background method for atmospheric OH measurements by laser-induced fluorescence: characterisation and observations from the UK and China

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Abstract. Hydroxyl (OH) and hydroperoxy (HO₂) radicals are central to the understanding of atmospheric chemistry. Owing to their short lifetimes, these species are frequently used to test the accuracy of model predictions and their underlying chemical mechanisms. In forested environments, laser-induced fluorescence–fluorescence assay by gas expansion (LIF–FAGE) measurements of OH have often shown
15 substantial disagreement with model predictions, suggesting the presence of unknown OH sources in such environments. However, it is also possible that the measurements have been affected by instrumental artefacts, due to the presence of interfering species that cannot be discriminated using the traditional method of obtaining background signals via modulation of the laser excitation wavelength (“OHwave”). The
20 interference hypothesis can be tested by using an alternative method to determine the OH background signal, via the addition of a chemical scavenging prior to sampling of ambient air (“OHchem”). In this work, the Leeds FAGE instrument was modified to include such a system to facilitate measurements of OHchem, in which propane was used to selectively remove OH from ambient air using an inlet pre-injector (IPI). The IPI system was characterised in detail, and it was found that the system did not reduce the instrument sensitivity
25 towards OH (<5% difference to conventional sampling), and was able to efficiently scavenge external OH (>99%) without the removal of OH formed inside the fluorescence cell (<5%). Tests of the photolytic interference from ozone in the presence of water vapour revealed a small but potentially significant interference, equivalent to an OH concentration of $\sim 4 \times 10^5$ molecule cm⁻³ under typical atmospheric conditions of [O₃] = 50 ppbv and [H₂O] = 1%. Laboratory experiments to investigate potential interferences
30 from products of isoprene ozonolysis did result in interference signals, but these were negligible when extrapolated down to ambient ozone and isoprene levels. The interference from NO₃ radicals was also tested but was found to be insignificant in our system. The Leeds IPI module was deployed during three separate field intensives that took place in summer at a coastal site in the UK, and both in summer and winter in the megacity Beijing, China, allowing for investigations of ambient OH interferences under a wide range of
35 chemical and meteorological conditions. Comparisons of ambient OHchem measurements to the traditional



OHwave method showed excellent agreement, with OHwave vs OHchem slopes of 1.05–1.16 and identical behaviour on a diel basis, consistent with laboratory interference tests.

1 Introduction

The removal of pollutants and greenhouse gases in the troposphere is dominated by reactions with the hydroxyl radical (OH), which is closely coupled to the hydroperoxy radical (HO₂). Comparisons of the levels of OH and HO₂ observed during field campaigns to the results of detailed chemical box models serve as a vital tool to assess our understanding of the underlying chemical mechanisms involved in tropospheric oxidation. Laser-induced fluorescence–fluorescence assay by gas expansion (LIF–FAGE) measurements of OH in forested environments have often been considerably higher than those predicted by models (Carslaw et al., 2001; Lelieveld et al., 2008; Ren et al., 2008; Hofzumahaus et al., 2009; Stone et al., 2011; Whalley et al., 2011; Wolfe et al., 2011). The difficulty in simulating radical concentrations in such environments has prompted a multitude of theoretical (Peeters et al., 2009; da Silva et al., 2010; Nguyen et al., 2010; Peeters and Muller, 2010; Peeters et al., 2014), laboratory (Dillon and Crowley, 2008; Hansen et al., 2017), and chamber (Paulot et al., 2009; Crouse et al., 2011; Crouse et al., 2012; Wolfe et al., 2012; Fuchs et al., 2013; Fuchs et al., 2014; Praske et al., 2015; Teng et al., 2017; Fuchs et al., 2018) studies to help explain the sources of the measurement–model discrepancy, through detailed investigations of the mechanism of isoprene oxidation under low NO_x conditions, as well as other biogenic volatile organic compounds (BVOCs) (Novelli et al., 2018). However, another hypothesis is that the LIF measurements have, at least in part, suffered from an instrumental bias in these environments due to interfering species.

Early LIF measurements of OH suffered from significant interferences due to laser-generated OH from ozone photolysis in the presence of water vapour (Hard et al., 1984). While this effect has been reduced in going from 282 to 308 nm laser excitation of OH, it may still be significant, especially at night or with the use of multi-pass laser setups (e.g., up to $\sim 4 \times 10^6$ molecule cm⁻³ in Griffith et al. (2016)). Laboratory experiments conducted by Ren and co-workers using the Pennsylvania State University (PSU) LIF instrument showed negligible interferences in OH detection for a range of candidate species: H₂O₂, HONO, HCHO, HNO₃, acetone, and various RO₂ radicals (Ren et al., 2004). Observations of OH during the PROPHET (Program for Research on Oxidants: PHotochemistry, Emissions and Transport) field campaign in summer 1998, located in a mixed deciduous forest in Michigan, USA, revealed unusually high nighttime OH concentrations ($\sim 1 \times 10^6$ molecule cm⁻³) but measurement interferences were ruled out (Faloona et al., 2001).

However, the results of more recent studies conducted in forested environments have meant that interferences in the measurement of OH by LIF–FAGE have been revisited. The usual background method of this technique, where the laser wavelength is scanned off-resonance from an OH transition (“OHwave”), does not discriminate between ambient (i.e., “real”) OH and either OH formed inside the FAGE cell (e.g., laser- or surface-generated OH, or via unimolecular decomposition in the gas phase to form OH), or fluorescence from other species at $\lambda \sim 308$ nm (e.g., naphthalene, SO₂), although it is possible to correct for such effects providing the interference has been previously characterised (Martinez et al., 2004; Ren et al.,



2004; Griffith et al., 2013; Fuchs et al., 2016). There is an alternative, chemical method (“OHchem”) for
obtaining the OH background signal in LIF instruments that allows for interference signals to be determined
without their prior characterisation, to rule out possible artefacts from unknown species. The OHchem
75 method involves the addition of a high concentration of an OH scavenger, such as perfluoropropene (C₃F₆)
or propane, just before the FAGE inlet. Ambient OH is quickly titrated away by fast reaction with the
scavenger, but any interference should remain in the fluorescence signal, although this must be corrected for
reaction of any internally generated OH with the scavenger inside the FAGE cell.

Several LIF–FAGE groups have now made efforts to validate ambient OH measurements through
80 incorporation of the alternative OHchem technique, which was first applied for continuous OH measurements
by (Mao et al., 2012). Since then, field studies of OH measurement interferences have been conducted in
forested (Griffith et al., 2013; Novelli et al., 2014a; Feiner et al., 2016; Novelli et al., 2017), rural (Fuchs et
al., 2017; Tan et al., 2017), suburban (Tan et al., 2018; Tan et al., 2019), urban (Ren et al., 2013; Brune et
al., 2016; Griffith et al., 2016), and coastal (Novelli et al., 2014a; Mallik et al., 2018) locations. Substantial
85 improvement in measurement–model agreement has been possible when OH backgrounds were determined
chemically, especially in forested environments, suggesting that understanding of tropospheric oxidation
processes in such regions may be better than previously thought (Mao et al., 2012; Hens et al., 2014; Feiner
et al., 2016). This is further supported by the positive identification of two new OH interference candidates
in laboratory experiments, namely intermediates in alkene ozonolysis reactions, which may (Novelli et al.,
90 2014b; Novelli et al., 2017; Rickly and Stevens, 2018) or may not (Fuchs et al., 2016) be related to stabilised
Criegee intermediates (SCIs), and the NO₃ radical (Fuchs et al., 2016) although for all cases the observed
interferences cannot explain the magnitudes of the OH background signals under ambient conditions. The
trioxide species, ROOOH, has also been postulated to explain elevated OH backgrounds in LIF–FAGE
measurements made in forested regions (Fittschen et al., 2019).

95 However, it is not known whether other LIF instruments suffer the same levels of interference, which are
likely highly dependent on cell design and operating parameters, especially the residence time of air between
sampling and detection (Novelli et al., 2014a; Fuchs et al., 2016; Rickly and Stevens, 2018). Considering the
bespoke nature of LIF–FAGE instruments, those of different groups share the same main features but differ
in many aspects, such as inlet size and shape, or whether the laser crosses the detection axis once (i.e., single-
100 pass) or multiple times (multi-pass). As a result, the magnitude of any interference is likely to vary
significantly between different instruments. Because of this, a general recommendation of the 2015
International HO_x Workshop (Hofzumahaus and Heard, 2016) was that different groups should incorporate
their own chemical scavenger system for use in ambient OH measurements, and to test interferences in the
laboratory.

105 Following this recommendation, the Leeds ground-based FAGE instrument was modified to incorporate
a chemical scavenger system, through the addition of an inlet pre-injector (IPI). In this work, we describe the
design of the IPI system and its thorough characterisation in terms of sensitivity and the degree of external
and internal OH removal. Following this, we present the results of interference testing experiments performed



110 using the IPI system, in which we investigated interferences from $O_3 + H_2O$, isoprene ozonolysis, and NO_3 radicals. Finally, we demonstrate the use of the optimised IPI system for measurements of ambient OH made during three separate field campaigns in the UK and China, which encompassed a wide range of chemical and meteorological conditions.

2 Methodology

2.1 Overview of the Leeds ground-based FAGE instrument

115 The University of Leeds ground-based FAGE instrument, described in detail elsewhere (Creasey et al., 1997a; Whalley et al., 2010; Whalley et al., 2013), has participated in 24 intensive field campaigns since its initial deployment in 1996. Measurements of OH, HO_2 , and, more recently, RO_2 radicals (Whalley et al., 2013), have been made in a variety of locations, ranging from pristine marine boundary layer (Creasey et al., 2003; Whalley et al., 2010), tropical rainforest (Whalley et al., 2011), and polar (Bloss et al., 2007) environments, to coastal (Smith et al., 2006) and semi-polluted regions (Creasey et al., 2001), as well as urban areas (Heard et al., 2004; Emmerson et al., 2007) including a highly polluted megacity (Lee et al., 2016; Whalley et al., 2016).

125 Ambient OH is measured using laser-induced fluorescence. Briefly, ambient air is drawn through a 1.0 mm diameter pinhole in a conical turret inlet (4 cm length, 3.4 cm ID; Figure 1) at ~ 7 slm into a stainless steel fluorescence cell, held at ~ 1.5 Torr using a Roots blower (Leybold RUVAC WAU 1001) backed by a rotary pump (Leybold SOGEVAC SV200). An all solid-state laser system is used to excite OH via the $A^2\Sigma^+(v' = 0) \leftarrow X^2\Pi_{3/2}(v'' = 0)$ electronic transition at $\lambda = 308$ nm (HO_2 is measured by conversion to OH using NO, details below). The resultant fluorescence at 308 nm is detected by a micro-channel plate photomultiplier (MCP, Photek PMT325/Q/BI/G with 10 mm diameter photocathode) equipped with a 50 ns gating unit (Photek GM10-50) and a 2 GHz 20 dB gain amplifier (Photek PA200-10), and the signal analysed by gated photon counting (Whalley et al., 2010). The background signal is normally obtained by scanning the laser wavelength off-resonance from the OH transition line, yielding the measurement commonly referred to as OHwave:

135
$$[OH_{wave}] = C_{OH} \times (S_{online}^{OH} - S_{offline}^{OH})$$
$$= C_{OH} \times S^{OH} \tag{1}$$

where C_{OH} is the instrument calibration factor for OH, and S_{online}^{OH} and $S_{offline}^{OH}$ are the OH LIF signals at on- and off-resonance wavelengths, respectively. Similarly, the alternative measurement known as OHchem is defined as:

140
$$[OH_{chem}] = C_{OH} \times (S_{online}^{OH} - S_{online, scavenger}^{OH})$$
$$= C_{OH} \times S_{scavenger}^{OH} \tag{2}$$



145 where $S_{\text{online, scavenger}}^{\text{OH}}$ is the OH signal measured at an on-resonance wavelength but in the presence of a scavenger.

HO₂ is detected via its conversion to OH following the addition of NO (BOC, 99.95% and Messer, 99.95%). Although not reported here, RO₂ radicals are measured using the RO_xLIF method (Fuchs et al., 2008; Whalley et al., 2013), in which their reactions with NO and CO (BOC, 5% in N₂ and Messer, 10% in N₂) result in conversion initially to OH and subsequently to HO₂ that is then detected as described above.
150 The NO and CO are delivered using mass flow controllers (MFC, MKS Instruments 1179A series), which, unless otherwise stated, were also used to control all other gas flows described in this work. The Leeds FAGE instrument features two fluorescence cells, where laser light (~10–20 mW at 308 nm, supplied at a pulse repetition frequency of 5 kHz via an optical fibre) enters each cell in series. For normal operation in the field, the first cell (HO_x) measures OH and HO₂ (low NO flow, 5 sccm; RO₂ interference minimised) sequentially,
155 while the second cell (RO_x) measures HO₂* (high NO flow, 50 sccm; RO₂ interference maximised) and then total RO₂ (Fuchs et al., 2008; Whalley et al., 2013).

Calibration of the FAGE instrument is achieved by supplying known radical concentrations via a turbulent flow tube (known in Leeds as the “wand”) held at ~45° to the instrument inlet, where OH and HO₂ are formed in a 1:1 ratio (Fuchs et al., 2011) by the photolysis of water vapour at 184.9 nm using a Hg(Ar) pen-ray lamp
160 (LOT LSP035) in an excess flow (40 slm) of humidified ultra-high purity air (BOC, BTCA 178 and Messer, 20.5% O₂ in N₂). Chemical actinometry is performed via the photolysis of N₂O (BOC, medical grade 98%) to measure the product of lamp flux and photolysis exposure time to enable calculation of radical concentrations (Edwards et al., 2003; Faloon et al., 2004). The calibration of OH using the water vapour photolysis method has been validated by comparison with other methods, for example the kinetic decay of
165 hydrocarbons (Winiberg et al., 2015).

2.2 Inlet pre-injector (IPI) design

The Leeds inlet pre-injector (Figure 1) is similar in concept to the design of Mao et al. (2012) and consists of a 4.0 cm length, 1.9 cm ID perfluoroalkoxy (PFA) cylinder embedded inside an aluminium housing, which seals to the FAGE cell via an O-ring base. The scavenger is injected into the centre of the PFA flow tube via
170 four 0.25 mm ID needles, 4.0 cm above the FAGE inlet. The low bore capillary tubing increases the pressure inside the needles, which facilitates mixing of the scavenger into the ambient air stream. In this work propane (BOC, research grade 99.95% and Messer, 99.995%) was used as the main OH chemical scavenger, with similar results (see section 3.1.2) obtained for C₃F₆ (Sigma-Aldrich, 99%). Based on previous investigations of OH interferences (Stevens et al., 1994; Dubey et al., 1996; Faloon et al., 2001; Ren et al., 2004; Mao et al., 2012; Griffith et al., 2013), C₃F₆ was used initially as it reacts quickly and selectively with OH ($k_{298} = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Sander et al., 2011)), and does not contain any hydrogen atoms which could serve as a source of laser-generated OH via abstraction by O(¹D) atoms (Stevens et al., 1994; Dubey et al., 1996). However, C₃F₆ must be diluted in an inert gas before it can be flowed through MFCs, and its availability in the UK became limited in 2015. Following Novelli et al. (2014a), we therefore used propane for most



180 laboratory experiments and all ambient measurements, despite the fact that it reacts more slowly with OH
($k_{298} = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Sander et al., 2011)).

As shown in Figure 2, the scavenger (0–50 sccm) is diluted in a flow of N₂ (500 sccm, BOC, 99.998%)
prior to injection, which is controlled using a solenoid valve (Metron Semiconductors). Any dead volume
after the valve is purged continuously by the N₂ dilution flow, using a narrow-bore injector inserted through
185 the tee after the valve, with the injector tip placed as close to the valve orifice as possible. This enables fast
flushing of the system to optimise the response time before and after scavenger injection. Incorporation of
the purge system resulted in pre- and post-injection stabilisation times on the order of seconds (data not
shown), minimising data loss. The valve state and scavenger flow over the course of the data acquisition
cycle are controlled using a custom program nested within the FAGE software.

190 To reduce radical wall losses, excess ambient air is drawn through the IPI to generate a sheath flow, via
four ports spaced evenly around the flow tube housing as shown in Figure 1. This minimises the FAGE
sampling of air from near the walls of the cylinder, housing, and turret. The total flow rate through the IPI is
32 slm, of which 7 slm is sampled by the FAGE cell and the remainder of the flow is maintained by a vacuum
pump (Agilent Technologies IDP-3 Dry Scroll Pump) and measured volumetrically using a rotameter
195 (Brooks 2520, 4–50 L min⁻¹).

During interference testing experiments using the IPI system (section 3.2), ozone and water vapour
concentrations were measured using a commercial UV absorption instrument (Thermo Environmental
Instruments Inc. 49C) and a chilled mirror dew point hygrometer (General Eastern 1311DR sensor and 4×4
Optica), respectively.

200 2.3 Field measurement sites

Ambient measurements of OH_{wave} and OH_{chem} were made using the Leeds IPI–FAGE instrument during
three separate intensive field campaigns, in different locations and seasons. This allowed for the investigation
of potential OH interferences under markedly contrasting conditions. For all three field campaigns,
measurements of OH, HO₂, and partially speciated RO₂ were made using the Leeds FAGE instrument (4 m
205 above ground level), operated in the sequential detection modes described in section 2.1 (Whalley et al.,
2013). Total OH reactivity, k'_{OH} , was also measured, using the laser flash photolysis–LIF instrument
described in detail by (Stone et al., 2016). A range of supporting chemical, aerosol, and meteorological
parameters were measured, with instruments situated either in buildings or shipping containers at each of the
two sites. Gas phase chemical observations included water vapour, NO_x, NO_y, O₃, CO, SO₂, HONO, HCHO
210 (Cryer, 2016), ClNO₂, VOCs, and OVOCs. Photolysis rates (J) for a variety of species, including O₃ (→
O(¹D)), NO₂, HCHO, HONO, and ClNO₂, were measured using a 2π spectral radiometer (2π actinic receiver
optic (Meteorologie Consult GmbH) coupled to an Ocean Optics QE Pro spectrometer), and $J(\text{O}^1\text{D})$ was also
measured using a 2π filter radiometer (Meteorologie Consult GmbH) (Bohn et al., 2008). The meteorological
and chemical conditions, including some example VOCs, encountered during each campaign are summarised
215 in Table 1 and discussed in further detail below.



220 The first deployment of the Leeds IPI was during the ICOZA (Integrated Chemistry of OZone in the Atmosphere) project, which took place in July 2015, at the Weybourne Atmospheric Observatory (WAO), Weybourne, located on the North Norfolk Coast, UK (52°57'02''N, 1°07'19''E, 15 m asl). The WAO is a Global Atmospheric Watch (GAW) Regional station, and the site is impacted by a range of contrasting air masses, from clean Arctic air to processed emissions from the UK (e.g., London, which is located ~180 km SSW of the observatory) and Northern Europe. The aim of this field campaign was to improve understanding of ozone chemistry through integrated measurements of $P(\text{O}_3)$, the chemical or *in situ* ozone production rate (OPR) (Cazorla and Brune, 2010; Cazorla et al., 2012), with comparisons to a range of other observational and model approaches.

225 In general, the ICOZA campaign was characterised (Table 1) by moderate temperatures (16 °C median), high humidity (RH ~ 80%), and strong wind speeds (~6 m s⁻¹), as might be expected at a temperate, coastal location in the summertime. The predominant wind sector, based on wind direction measurements at the site, was westerly (~30%), followed by southwesterly (~20%) and southerly (~15%). Back-trajectory analysis showed that during IPI sampling periods, the site was predominantly under the influence of Atlantic air (Cryer, 2016). These air masses had spent a considerable amount of time (~1 day) over the UK, often encountering emissions from urban areas, which underwent photochemical aging during their transport to the WAO site. Overall, the levels of pollution observed at the site were moderate, and the lowest of the three field campaigns discussed in this work (Table 1), and levels of isoprene were low. However, ozone mixing ratios were relatively high, with a diel-average maximum of ~40 ppbv, driven in part by strong UV and near-UV radiation.

235 The Leeds IPI was deployed during another two campaigns at the Institute of Atmospheric Physics (IAP, 39°58'36.06''N, 116°22'53.69''E), an urban site in Beijing, China, during winter (November–December) 2016 and summer (May–June) 2017, as part of the AIRPRO (an integrated study of AIR pollution PROCesses in Beijing) project. AIRPRO is part of the wider APHH (Air Pollution and Human Health in a Chinese megacity) project (Shi et al., 2018), a joint UK–China programme. The aims of AIRPRO included the assessment of how pollutants are transformed and removed through transport, chemical, and photolytic processes, with a particular emphasis on the identification of the dominant oxidative degradation pathways (i.e., the relative importance of reactions with OH, NO₃, and O₃). The AIRPRO project allowed for the assessment of OH measurement interferences under the highly polluted conditions of the megacity Beijing, situated in the heavily industrialised North China Plain. In winter, the site is impacted by urban and regional anthropogenic emissions, in particular those from the combustion of fossil fuels for residential heating. During summer, the site is subject to additional biogenic influences, and strong photochemical activity results in high rates of ozone production.

240 For both AIRPRO field intensives, the predominant wind sectors were westerly and southerly/southeasterly, which generally result in higher pollutant concentrations (Chen et al., 2015). Indeed, the two campaigns were subject to high pollutant concentrations, as illustrated by the elevated levels of NO₂, CO, propane, benzene, and k'_{OH} , many of which were over an order of magnitude higher than ICOZA (Table



1). In addition, the biogenic influence during summer is clear from the relatively high isoprene concentrations observed, ~0.4 ppbv on average but reaching up to 7.9 ppbv, a level considerably higher than those observed in some forested environments. Despite similar $J(\text{O}^1\text{D})$ values between ICOZA and AIRPRO summer, the higher VOC loadings during the latter resulted in increased production of ozone (90 ppbv diurnally-averaged maximum). In contrast, AIRPRO winter was characterised by small ozone mixing ratios (15 ppbv diurnal maximum), as a consequence of high NO levels (median 22 ppbv) and weak UV radiation. In summer, NO levels were high in the morning (~14 ppbv at 06:00 China Standard Time (CST)) but surprisingly low in the afternoon, with diel-average median levels of ~0.5 ppbv (15:00–18:00 CST).

For all ambient observation periods, the IPI data acquisition cycle consisted of 5 minutes of online wavelength and 30 seconds of offline wavelength (spectral background) integration, where the online period was split into 2 minutes of OH measurements and 2 minutes of propane addition to the IPI flow tube (chemical background), followed by 1 minute of HO₂ measurements (by the addition of NO to the FAGE cell). In terms of instrumental operation, the only difference between ICOZA and the AIRPRO campaigns was the use of different propane flows in the IPI. The propane concentration in the IPI flow tube was ~110 ppmv ($k'_{\text{OH}} \sim 3000 \text{ s}^{-1}$, $\tau_{\text{OH}} \sim 0.3 \text{ ms}$) during ICOZA and AIRPRO winter but, after internal removal experiments revealed that the propane level could be increased further (see section 3.1.3), a ten-fold higher concentration (~1100 ppmv), resulting in a concomitant reduction in the OH lifetime, was used for the AIRPRO summer campaign. On one day with high ozone (up to ~80 ppbv) and moderate isoprene (~0.5–1 ppbv) levels, the propane mixing ratio was reduced to ~110 ppmv, but this had no observable effect on the background signals obtained for the summer data. All ambient OHwave data presented here have been corrected for the known interference from O₃ in the presence of H₂O vapour (see section 3.2.1).

3 Results

3.1 IPI characterisation

3.1.1 Sensitivity

The presence of additional surfaces in the IPI system may result in radical wall losses and therefore reduce the overall FAGE instrument sensitivity. To test for potential OH losses in the IPI flow tube, OH radicals were generated using a 184.9 nm Hg lamp placed at ~19 cm from the instrument inlet, so that ambient air with elevated radical concentrations (~2–7 × 10⁷ molecule cm⁻³) was sampled, alternating between IPI and non-IPI sampling (Figure 3), where for the latter the entire IPI assembly was removed. The dominant source of OH was the photolysis of ambient water vapour at 184.9 nm. In these experiments, the Hg lamp was placed sufficiently far away from each inlet within a large tent enclosure on the container roof, such that it could be assumed that OH concentrations were uniform in the region the inlet sampled from. Otherwise, the difference in inlet height between IPI and non-IPI sampling may have resulted in different OH concentrations being sampled, e.g., due to differences in O₃ absorption at 184.9 nm (O₃ has a high cross-section at this wavelength), which would affect the light flux at the point of sampling and hence the concentration of OH generated. Since



290 ambient variability (e.g., in NO_x levels) also affects the atmospheric radical concentrations, the IPI/non-IPI
cycle was repeated several tens of times on three different days within the tent enclosure to ensure sufficient
averaging of the results. Any differences in wind speed or direction during the different days are not important
because of the tent enclosure. Based on the averages for each set of repeat measurements in Figure 3, these
experiments yield a mean $\pm 2\sigma$ IPIoff/IPIon ratio of 1.043 ± 0.023 , i.e., a $<5\%$ sensitivity reduction due to
the presence of the IPI. While HO_2 loss was not tested, the relative sensitivity is assumed to be closer to unity
since it is less reactive than OH. In either case, the correction is smaller than the total instrumental uncertainty
295 ($\sim 26\%$ at 2σ), and as such no corrections were applied to OH or HO_2 calibration factors for the final workup
of ambient data collected during IPI sampling periods.

The lack of OH loss in the IPI system is further supported by another test conducted in the field during
the summer 2017 AIRPRO campaign, where on one day of the campaign, sequential measurements of
OHwave were taken with and without the IPI assembly present. While this was not a formal intercomparison,
300 the summer 2017 campaign provided ideal conditions to assess IPI losses, considering the very high radical
concentrations observed (OH frequently $>1 \times 10^7$ molecule cm^{-3}) in Beijing and thus a good signal-to-noise
ratio. The results of this experiment are shown for OH in Figure 4. It can be seen that if no correction for a
reduction in sensitivity reduction is applied, adjacent IPIoff and IPIon periods of data are qualitatively in
agreement, with no discontinuities in the temporal profile, implying that IPI sensitivity loss is close to zero
305 under field operating conditions. Similar results were obtained for HO_2 (data not shown).

3.1.2 External OH removal

The external OH removal efficiency in the IPI system is controlled by the injection height, the choice of
scavenger (i.e., the rate coefficient of the reaction of scavenger with OH), the scavenger and N_2 dilution gas
flows delivered to the injectors, as well as the sheath flow. A key requirement here is efficient mixing of the
310 scavenger into the ambient air stream, which is difficult considering the fast flow rate and hence short
residence time of air in the IPI flow tube. Additionally, it is important to consider that some reaction of the
scavenger may occur inside the fluorescence chamber (internal OH removal, section 3.1.3). This would give
rise to a positive bias in ambient OH concentration measurements made using the OHchem method, as
internal OH removal could result in loss of interfering OH and therefore an apparent reduction in the true
315 background signal.

External OH removal experiments were performed by supplying known concentrations of OH and HO_2
to the instrument using the calibration wand described in section 2.1. However, in contrast to normal
calibration procedures, where the wand is held at 45° to the pinhole (to overfill the pinhole and minimise
sampling of pockets of air which may have been in contact with the metal pinhole surface), IPI
320 characterisation experiments were performed with the wand positioned parallel to the direction of flow within
the IPI (i.e., 90° relative to the plane of the pinhole), with a distance of ~ 3 cm between the wand exit and the
PFA flow tube. The high flow through the calibration wand (40 slm) ensured that an excess of calibration
gas was delivered to the IPI system (sample flow ~ 32 slm).



The external OH removal efficiency ($RE_{\text{external}}^{\text{OH}}$) may be calculated from the proportion of OH remaining
325 ($R_{\text{external}}^{\text{OH}}$) after injection of the scavenger, obtained from the ratio of the OH signals in the presence
($S_{\text{scavenger}}^{\text{OH}}$) and absence (S^{OH}) of the scavenger:

$$R_{\text{external}}^{\text{OH}} (\%) = 100 \times S_{\text{scavenger}}^{\text{OH}} / S^{\text{OH}} \quad (3)$$

$$RE_{\text{external}}^{\text{OH}} (\%) = 100 - R_{\text{external}}^{\text{OH}} \quad (4)$$

330

Initial tests included variation of the N_2 dilution flow, however the OH removal efficiency was generally low
(data not shown), likely due to poor mixing of the scavenger into the sampled air when the flow rate from
the injector is small. As a result, the N_2 dilution was set to the maximum flow of the MFC used (0.5 slm) for
all subsequent experiments. Any further dilution of the ambient air stream would result in a loss of sensitivity
335 towards the detection of radicals, however, at 0.5 slm the dilution flow is virtually negligible compared to
the total flow rate in the IPI system (32 slm). In other preliminary experiments, the scavenger was injected
closer to the FAGE inlet (1.0 and 2.5 cm), but this also resulted in poor external OH removal owing to the
shorter residence time between scavenger injection and FAGE sampling.

The scavenging efficiency was determined for both propane and C_3F_6 , with good agreement between the
340 two scavengers. Figure 5 shows the remaining OH signal as a function of the OH reactivity ($k'_{\text{OH}} = k_{\text{OH}+\text{scavenger}}$
[scavenger]) calculated in the flow tube, which normalises the scavenger concentrations according to their
different reaction rates with OH. The observed removal efficiency is in broad agreement with the theoretical
scavenging efficiency, based on the residence time in the flow tube (~20 ms, assuming plug flow) and
assuming perfect mixing, suggesting that in the Leeds IPI system the scavenger is well mixed into the gas
345 sampled by the FAGE cell. An optimum removal of virtually 100% (OH remaining $\pm 2\sigma = 0.030 \pm 0.091\%$)
was observed at $k'_{\text{OH}} \sim 3000 \text{ s}^{-1}$, equivalent to ~110 ppmv ($2.7 \times 10^{15} \text{ molecule cm}^{-3}$) propane. This scavenger
concentration was used for measurements of OHchem during the summer 2015 ICOZA project and winter
2016 AIRPRO project. For the summer 2017 AIRPRO project, a ten-fold higher scavenger concentration
was used (~1100 ppmv propane), after internal removal experiments revealed no loss of internal OH at this
350 higher concentration, as discussed in detail in the next section.

3.1.3 Internal OH removal

Internal removal of OH was quantified by Mao et al. (2012) after forming OH inside the PSU ground-FAGE
cell using a Hg lamp, and comparing the OH signal with and without the presence of the scavenger (C_3F_6),
added externally in the IPI system. It was found that most of the internal removal occurred in the instrument
355 inlet, rather than in the OH detection axis, with a total loss of ~20%. Internal removal was not tested in the
laboratory by Novelli et al. (2014a) for the Max Planck Institute for Chemistry (MPIC) FAGE instrument,
but instead they limited the scavenger (propene and propane) concentration such that the external OH removal
efficiency was < 95%, to minimise possible reaction of the scavenger with OH inside the fluorescence cell.
However, during ambient, nighttime tests (constant atmospheric OH concentration assumed), no change in



360 the OH background signal was observed after increasing the scavenger concentration by a factor of seven, providing evidence for a lack of internal removal (Novelli et al., 2014a).

In the present study, a novel approach was devised to quantify internal removal of OH in the Leeds IPI-FAGE instrument. First, under otherwise identical experimental conditions to those for external OH removal tests, sufficient CO (75 sccm, 95 ppmv) was added to the calibration wand to verify that the OH formed (alongside HO₂) from the photolysis of water vapour was almost quantitatively converted to HO₂ (98.0 ± 0.4%, data not shown). Secondly, in addition to the calibration wand CO flow, a high flow of NO (50 sccm) was injected inside the FAGE cell, with the injector tip positioned centrally just below the turret pinhole, to reconvert the HO₂ back to OH for LIF detection; these experimental conditions ensured a fairly high HO₂-to-OH conversion efficiency of approximately 30%. In this manner, OH was only generated inside the FAGE cell, and not in the IPI flow tube, such that any change in the fluorescence signal could be attributed to internal reaction of OH with propane, rather than reaction in the flow tube. The procedure for determination of internal OH removal bears some resemblance to that used for ambient detection of RO₂ using the RO_xLIF technique (Fuchs et al., 2008; Whalley et al., 2013), i.e., the external conversion of all radical species to HO₂ before internal conversion to OH within the fluorescence cell.

375 The internal OH removal efficiency ($RE_{\text{internal}}^{\text{OH}}$) was quantified in an analogous manner to the external scavenging efficiency, using the total fluorescence signal in the presence ($S^{\text{HOx}}_{\text{scavenger}}$) and absence (S^{HOx}) of the scavenger:

$$R_{\text{internal}}^{\text{OH}} (\%) = 100 \times S^{\text{HOx}}_{\text{scavenger}} / S^{\text{HOx}} \quad (5)$$

380 $RE_{\text{internal}}^{\text{OH}} (\%) = 100 - R_{\text{internal}}^{\text{OH}} \quad (6)$

Figure 6 shows a time series of the LIF signal during two example internal removal experiments. Here, the LIF signal represents the sum of signals from OH and HO₂, since they are produced in a 1:1 ratio (Fuchs et al., 2011) in the calibration wand. For both of the propane mixing ratios used, which were shown to result in near complete external OH removal in section 3.1.2, there was no obvious decrease in the LIF signal, indicating no significant internal removal of OH. The average ± 2σ internal OH removal observed for repeat experiments was -0.5 ± 1.3% (Table 2) at a propane mixing ratio of ~110 ppmv (ICOZA and AIRPRO winter conditions). For repeat experiments at the higher propane mixing ratio used during the AIRPRO summer field campaign (~1100 ppmv), the internal removal was still very small, and almost insignificant (2.8 ± 2.3%, Table 2). The observed internal OH removal may be compared to that which might be expected theoretically. In the ambient pressure flow tube, a propane mixing ratio of 1100 ppmv equates to $k'_{\text{OH}} = 30,000 \text{ s}^{-1}$, but this is a factor of 760/1.5 lower in the detection cell (i.e., the ratio of ambient to cell pressure), 59 s⁻¹ (assuming constant gas density and no change in the OH + propane rate coefficient). Under normal operation, NO injection occurs 10.5 cm below the pinhole, and 7.5 cm away from the laser axis (i.e., total of 18 cm between the pinhole and detection volume), with a residence time of 0.9 ms between NO injection and OH detection (Creasey et al., 1997b; Whalley et al., 2013). The gas likely slows down between pinhole sampling and NO



injection, but assuming a constant gas velocity, the residence time between the pinhole and the laser axis is estimated at ~2 ms. Based on this, an internal OH removal of efficiency ~12% is calculated, which is higher than observed, likely because the assumption of constant gas velocity is invalid (i.e., the real residence time is closer to ~1 ms) and mixing between HO₂ and NO from the injector is not instantaneous. However, it should be noted that this calculation also neglects the fact that the density is higher in the jet, or the perturbation to normal flow caused by moving the NO injector close to the pinhole.

3.2 Interference testing experiments

3.2.1 O₃ + H₂O vapour

In LIF-FAGE instruments, there is a known interference due to laser-generated OH from ozone photolysis in the presence of water vapour (Fuchs et al., 2016; Griffith et al., 2016; Tan et al., 2017). This interference was quantified by (Whalley et al., 2018) and characterised in further detail in the present work. In these experiments, ozone was generated from the 184.9 nm photolysis of oxygen in a 12–20 slm flow of zero air using a Hg(Ar) pen-ray lamp (LOT LSP035). Another 12–20 slm of zero air was humidified using a water (HPLC grade) bubbler. The two zero air flows were combined and delivered to the calibration wand, from which the IPI sampled in a manner analogous to the experiments conducted to investigate external and internal OH removal discussed above. Ozone mixing ratios in the range 0–2.5 ppmv were generated by varying the Hg lamp current (0–21 mA), while water vapour levels in the range 0.1–1.0% were produced by varying the flow through the bubbler, or by bypassing it completely, and the total flow (32 slm) was compensated by changing the dry zero air flow. Laser power (LP) at 308 nm was varied in the range 3–17 mW by varying the ratio of acetone:water in a cuvette placed before the fibre launcher that is used to send laser light to the detection cells.

Figure 7 shows the results of O₃ + H₂O vapour interference tests. It can be seen that the interference signal (OH_{int} = OH_{wave} – OH_{chem}) is linear in both ozone (panel (a)) and water vapour (panel (b)) mixing ratios. The quadratic dependence of the interference signal on laser power (panel (c)) in terms of raw count rates indicates that the interference originates from a two-photon process, as expected. However, since OH data are normalised to laser power, the equivalent OH concentrations are linear with respect to laser power. Thus overall, OH_{int} is linear in ozone, water vapour, and laser power. Normalisation of the slope in panel (a) yields the relation:

$$[\text{OH}_{\text{int}}] = (520 \pm 140) \text{ molecule cm}^{-3} \text{ ppbv}^{-1} \%^{-1} \text{ mW}^{-1} \times [\text{O}_3] \times [\text{H}_2\text{O}] \times \text{LP} \quad (7)$$

where [O₃], [H₂O], and LP are in units of ppbv, %, and mW, respectively. Under typical atmospheric conditions of [O₃] = 50 ppbv and [H₂O] = 1%, and a typical instrument laser power of 15 mW, the interference signal is equivalent to an OH concentration of $3.9 \times 10^5 \text{ molecule cm}^{-3}$. This signal is slightly smaller than the instrumental limit of detection (LOD) of $\sim 7 \times 10^5 \text{ molecule cm}^{-3}$ at a signal-to-noise ratio (SNR) of 2,



but nonetheless it was used to correct the ambient OHwave data presented in section 3.3, using co-located measurements of ozone and water vapour.

3.2.2 Isoprene ozonolysis

435 To test for interferences from isoprene (ISO) ozonolysis products, isoprene (~16 ppmv) and ozone (~1.8
ppmv) were mixed in the calibration wand and the scavenger (propane, PROP) was injected into the IPI flow
tube. The propane concentrations were set to those used for ambient OHchem measurements, such that the
tests were representative of normal atmospheric sampling (i.e., to test whether an interference signal would
440 remain in ambient data). However, to generate sufficient OH signal for quantitative analysis, ozone and
isoprene were introduced at concentrations that far exceeded their typical ambient levels (Table 3). Unlike
previous tests of interferences from alkene ozonolysis (Novelli et al., 2014b), low [O₃]:[ISO] ratios were used
to suppress the signal contribution from the atmospheric (real) OH generated by ozonolysis (i.e., isoprene
acted as an additional OH scavenger). To allow sufficient time for steady-state conditions to develop, the IPI
445 did not sample from the calibration wand directly, but instead a 30 cm flow tube (ID ~ 19 mm) was used
to extend the IPI (which sampled wand gas at the normal IPI flow rate of ~32 slm, $\tau \sim 0.15$ s).

Time series of the interference testing experiments conducted using the IPI are shown in Figure 8. In panel
(a), no isoprene is added, but due to ozone photolysis in the presence of high [H₂O] (0.73%) an interference
signal (OH_{int}) is observed (i.e., signal in the presence of propane is higher than the offline signal). The
magnitude of this signal (OH_{int} ~ 1.0×10^7 molecule cm⁻³) yields a scale factor of 510 ± 270 molecule cm⁻³
450 ppbv⁻¹ %⁻¹ mW⁻¹ when linearly extrapolated down from the measured [O₃], [H₂O], and LP, in agreement
with the 520 ± 140 molecule cm⁻³ ppbv⁻¹ %⁻¹ mW⁻¹ in equation (E7).

In panel (b), ozone and isoprene react under dry conditions, and an interference signal is observed again.
The low H₂O (0.07%) suppressed the O₃ + H₂O interference, such that this cannot explain the magnitude of
OH_{int} (~ 1.9×10^7 molecule cm⁻³, Table 3), suggesting that OH was formed internally from a reaction other
455 than O¹D + H₂O. Under high-humidity (H₂O ~ 1%) conditions (panel (c)), OH_{int} (~ 1.6×10^7 molecule cm⁻³)
was similar, but in this case the signal can be explained almost entirely by the O₃ + H₂O interference. Under
dry conditions but with a ten-fold higher concentration of propane (as used for the AIRPRO summer
campaign, panel (c)), the interference signal from panel (b) was reduced but remained elevated relative to the
offline signal (OH_{int} ~ 1.4×10^7 molecule cm⁻³), where again the contribution from O₃ + H₂O cannot explain
460 the discrepancy. The decrease in OH_{int} between panels (b) and (d) may be attributed to the suppression of
steady-state OH generated from ozonolysis, but the remaining signal implies that OH was also formed
internally in both cases. For the dry, low-propane experiment (panel (b)), the magnitude of the OH signal is
much higher than that calculated from a steady-state model (~ 1.4×10^6 molecule cm⁻³).

The suppression of the interference signal attributable to O₃/isoprene only (i.e., O₃ + H₂O corrected) by
465 the addition of water vapour (panel (c), H₂O ~ 1%) suggests that the internal OH may have been formed from
SCIs. The simplest C1 and C2 SCIs are known to react quickly with the water vapour dimer ($k \sim 4\text{--}7 \times 10^{-12}$
cm³ molecule⁻¹ s⁻¹ at 298 K for CH₂OO (Chao et al., 2015; Lewis et al., 2015)) and monomer ($k \sim 1\text{--}2 \times$



470 $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for *anti*-CH₃CHOO (Taatjes et al., 2013; Sheps et al., 2014; Lin et al., 2016)),
respectively. Reaction with the water vapour monomer was also shown to be relatively fast ($k \sim 1.2 \times 10^{-15}$
 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{\text{loss}} \sim 300 \text{ s}^{-1}$ at $\sim 1\% \text{ H}_2\text{O}$) for the ensemble of SCIs, including the C1 SCI, generated
from isoprene ozonolysis (Newland et al., 2015).

475 However, regardless of whether the signal observed at high propane is due to internally formed OH, which
may have originated from SCIs, the equivalent OH concentrations are negligible when extrapolated back to
ambient chemical conditions (Table 3). Assuming a linear dependence of the interference signal on both
ozone and isoprene, the interference (after O₃ + H₂O correction) is equivalent to $<10^2 \text{ molecule cm}^{-3}$ at the
ozone (10 ppbv) and isoprene (3.5 ppbv) levels measured in a low-NO_x, biogenic environment during the
Oxidants and Particle photochemical processes (OP3) campaign in Borneo, 2008 (Hewitt et al., 2010).
Similarly, the interference is calculated to be higher for the ozone (90 ppbv) and isoprene (7.9 ppbv) levels
during the summer AIRPRO campaign, but it is still $<10^3 \text{ molecule cm}^{-3}$. The insignificance of the
480 interference signal for atmospherically relevant O₃/alkene concentrations is consistent with the results of
previous interference experiments, for which equivalent OH concentrations of $\sim 3\text{--}4 \times 10^4$ (Novelli et al.,
2014b; Fuchs et al., 2016) and $\sim 4 \times 10^5 \text{ molecule cm}^{-3}$ (Rickly and Stevens, 2018) can be derived.

3.2.3 NO₃ radicals

485 Fuchs et al. (2016) found that, despite the absence of a hydrogen atom, NO₃ radicals were responsible for a
small OH interference signal in the Forschungszentrum Jülich (FZJ) LIF-FAGE instrument, equivalent to an
OH concentration of $1.1 \times 10^5 \text{ molecule cm}^{-3}$ per 10 pptv NO₃. The OH interference scaled linearly with
observed NO₃ mixing ratios but showed no dependence on inlet length, cell pressure, laser power, or
humidity, and the background signal did not change significantly in the presence of CO scavenger, suggesting
the OH was indeed being formed internally. It was postulated that the interference was a result of a
490 heterogeneous process involving NO₃ and H₂O adsorbed on instrument walls. Interference signals were also
observed in the detection of HO₂ and RO₂ radicals, equivalent to 1.0×10^7 and $1.7 \times 10^7 \text{ molecule cm}^{-3}$,
respectively, per 10 pptv NO₃.

To test for an NO₃ interference in OH measurements made by the Leeds FAGE instrument, NO₃ was
generated from the reaction of ozone and NO₂:

495



500 In these experiments, ozone was generated by flowing zero air (15 slm) past a Hg lamp (LOT LSP035). A
constant 0.5 slm flow of NO₂ (BOC, 2 ppmv) was diluted in 25 slm zero air and mixed with the zero air/ozone
flow as well as an additional zero air dilution flow of 10 slm, to yield a final mixing ratio of 20 ppbv. Gas
was delivered to the IPI system using the calibration wand, with a total residence time of 3.7 s for the O₃ +



505 NO₂ reaction. Ozone mixing ratios in the range 0–2.8 ppmv (after dilution) were generated by varying the current supplied to the Hg lamp. NO₃ radical mixing ratios in the range 0–90 pptv were calculated based on a box model with rate constants taken from the Master Chemical Mechanism (MCM; <http://mcm.leeds.ac.uk/MCM>) version 3.3.1 ($k_{R1} = 3.52 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{R2} = 1.24 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $k_{R3} = 0.045 \text{ s}^{-1}$). These experiments were performed under dry conditions (H₂O ~ 0.07%), such that only a small correction was applied for the O₃/H₂O interference.

510 The results of the NO₃ radical interference tests are shown in Figure 9. It can be seen that the equivalent OH signals were all $< 8 \times 10^5 \text{ molecule cm}^{-3}$, and almost always below the instrument LOD of $6.3 \times 10^5 \text{ molecule cm}^{-3}$ (SNR = 2). Unlike the dependence found by Fuchs et al. (2016), the interference signal does not increase linearly with NO₃. However, based on the point at the highest NO₃ mixing ratio of ~90 pptv, the interference is equivalent to an insignificant $\sim 6 \times 10^4 \text{ molecule cm}^{-3}$ at 10 pptv NO₃, or approximately half
515 of that observed by Fuchs et al. (2016). These experiments suggest that an interference from NO₃ radicals is not significant for the detection of OH using the Leeds ground-based FAGE instrument.

3.3 Ambient observations of OHwave and OHchem

3.3.1 ICOZA 2015

520 Figure 10 shows the overall intercomparison of OHwave (with O₃ + H₂O interference as given in Equation 7 subtracted) and OHchem measurements made during the ICOZA 2015 campaign. It is evident that the raw data (averaged for 4 minute periods) are quite noisy, but averaging to 1 h improves the precision and reveals a tight correlation, with the majority of points scattered around the line of 1:1 agreement. An orthogonal distance regression (ODR) fit (Boggs et al., 1987), which accounts for errors in both the y- and x- directions, to the hourly data yields a slope of 1.160 ± 0.058 (2σ) and a negative intercept on the order of the instrumental precision. In a similar manner, an unweighted least squares linear fit (not shown) gives a slope of 1.060 ± 0.065 , an intercept of $(0.5 \pm 1.5) \times 10^5 \text{ molecule cm}^{-3}$, and a correlation coefficient (R^2) of 0.992. Regardless
525 of the fit method, these results show that on average, the two OH measurements agree within the instrumental uncertainty of ~26% at 2σ .

530 Median hourly diurnal profiles of OHwave, OHchem, and $J(\text{O}^1\text{D})$, averaged over both IPI sampling periods, are shown in Figure 11. The two OH measurements exhibit virtually identical profiles, with peak values of $\sim 3 \times 10^6 \text{ molecule cm}^{-3}$ slightly before solar noon, and relatively high concentrations ($\sim 1\text{--}2 \times 10^6 \text{ molecule cm}^{-3}$) persisting into the early evening despite the concomitant falloff in $J(\text{O}^1\text{D})$. Nighttime levels were generally below $5 \times 10^5 \text{ molecule cm}^{-3}$. The variability in OH concentrations, shown only for OHchem for clarity, was high during both day and nighttime periods.

535 In Figure 10 it can be seen that some points lie substantially above the 1:1 line, especially for the 4 minute averaged raw data. It is possible that, despite the good overall agreement between the median diurnal profiles of OHwave and OHchem in Figure 11, OH_{hint} may have exhibited its own distinct diurnal profile, independent of atmospheric OH concentrations, for example if the interference signal was generated from a particular chemical species. However, the median diurnal profile of individual OH_{hint} measurements (= OHwave –



540 OHchem) in Figure 11 exhibits no obvious structure, with values scattered around zero and a mean $\pm 2\sigma$ value of $(0.3 \pm 3.3) \times 10^5$ molecule cm^{-3} , which is well below the LOD for individual OH measurements. Similarly, the average (OHwave – OHchem)/OHwave ratio (i.e., the contribution of interferences to the total OHwave signal) was zero within error (mean ± 2 standard errors (SE) = 0.03 ± 0.12).

545 Furthermore, OHwave and OHchem exhibit virtually identical behaviour when binned against various parameters (Woodward-Massey, 2018), including those previously implicated in LIF–FAGE measurement interferences, such as $J(\text{O}^1\text{D})$ (Feiner et al., 2016), temperature (Mao et al., 2012; Novelli et al., 2017), OH reactivity k'_{OH} (Mao et al., 2012), OH reactivity due to VOCs, and O_3 (Feiner et al., 2016; Novelli et al., 2017) and NO (Feiner et al., 2016) mixing ratios.

3.3.2 AIRPRO winter 2016

550 The overall agreement between the two measurements is presented in the correlation plot in Figure 12. As with ICOZA (Figure 10), a tight correlation is revealed after averaging the data to one hour, and all points are distributed evenly around the line of 1:1 agreement. ODR fitting yields an overall slope of 1.051 ± 0.039 and a negative intercept of a similar magnitude to the instrumental precision. An unweighted least squares linear fit (not shown) gives a slope of 0.997 ± 0.038 , an intercept of $(5.1 \pm 7.3) \times 10^4$ molecule cm^{-3} , and an R^2 of 0.97.

555 The two measurements exhibit the same profile on a diurnal basis (Figure 13), with a diel maximum of $\sim 3 \times 10^6$ molecule cm^{-3} occurring in the late morning due to the build-up of HONO overnight. At night, OHchem concentrations were close to the LOD ($< \sim 2 \times 10^5$ molecule cm^{-3}), while OHwave measurements were frequently negative, possibly as a result of over-subtraction of the $\text{O}_3/\text{H}_2\text{O}$ interference as this is subject to high uncertainty (Figure 7). The diurnal profile of OHint is scattered around zero with a mean $\pm 2\sigma$ difference of $(-0.9 \pm 2.7) \times 10^5$ molecule cm^{-3} , and the mean ± 2 SE contribution of interferences to the total signal was -0.02 ± 0.07 .

3.3.3 AIRPRO summer 2017

565 The intercomparison of OHwave and OHchem measurements for the AIRPRO summer campaign is shown in Figure 14. Consistent with ICOZA and the AIRPRO winter results, the 1 h data are scattered around the 1:1 line, with an overall ODR slope of 1.103 ± 0.017 . However, the intercept is more negative than for the other campaigns, which suggests that the $\text{O}_3/\text{H}_2\text{O}$ interference may have been overestimated, as it is during this campaign that the highest ozone mixing ratios (~ 90 ppbv diurnally-averaged maximum, Table 1) were encountered. Similarly, an unweighted least squares linear fit to the data (not shown) yields a slope of 1.111 ± 0.029 , an intercept of $(-3.8 \pm 1.7) \times 10^5$ molecule cm^{-3} , and an R^2 of 0.92 (data not shown).

570 Again, the two measurements follow the same diurnal profile (Figure 15), peaking in the afternoon at $\sim 1 \times 10^7$ molecule cm^{-3} with relatively high nighttime levels of $\sim 1-2 \times 10^6$ molecule cm^{-3} . As with ICOZA and the AIRPRO winter campaign, the OHint diurnal profile does not exhibit any obvious structure, with values scattered around zero and a mean $\pm 2\sigma$ difference of $(-1.6 \pm 4.1) \times 10^5$ molecule cm^{-3} . The mean ± 2 SE



575 (OH_{wave} – OH_{chem})/OH_{wave} ratio was -0.09 ± 0.10 . During AIRPRO, measured NO₃ mixing ratios reached up to ~100 pptv, such that the lack of significant nighttime OH interference signals is consistent with the results of NO₃ interference tests (section 3.2.3).

It can be seen from Figure 14 that there is a small cluster of points that lie significantly away from both the 1:1 and ODR regression lines, which are characterised by high OH_{wave} concentrations of $> 1.5 \times 10^7$ molecule cm⁻³. This finding was investigated further, with the results summarised in Figure 16. Above an OH_{chem} threshold of ~1.0–1.5 × 10⁷ molecule cm⁻³, the OH_{int} signal becomes significantly greater than zero and the instrument LOD, reaching ~3–5 × 10⁶ molecule cm⁻³ at OH_{chem} levels of around ~2 × 10⁷ molecule cm⁻³. However, these results should be treated with caution, since only a few points are available for which OH_{chem} was present at such high concentrations. The same behaviour was not observed for either
585 the AIRPRO winter or ICOZA campaigns, since OH_{chem} levels did not surpass 1 × 10⁷ molecule cm⁻³, but the analogous mean values at low OH_{chem} concentrations are in agreement with the AIRPRO summer results.

The above results suggest that in the Beijing summertime, the Leeds FAGE instrument is subject to an interference(s) at the highest OH levels, although its contribution of ~15–20% (Figure 16) is still below the instrumental accuracy of 26% at 2σ. This finding is consistent with the suggestion of (Fittschen et al., 2019) that ROOOH species, formed from RO₂ + OH reactions, generate an OH interference in LIF-FAGE instruments, since high OH levels would generate high RO₂ concentrations and favour this class of reaction. It is also possible that, for high ambient OH production rates, the scavenger cannot react with the sampled OH sufficiently quickly, leading to elevated but spurious OH_{chem} background signals. Although a modelling
595 study of the inlet chemistry would be required to fully assess this hypothesis, it is likely not the case considering that the propane concentration used during AIRPRO results in an OH lifetime of ~0.03 ms in the IPI flow tube, in comparison to a residence time of ~20 ms (i.e., ~700 OH lifetimes).

4 Discussion

The results from the three field campaigns that feature in this work demonstrate that the Leeds ground-based
600 FAGE instrument does not suffer from substantial interferences in the measurement of OH using the conventional, wavelength-modulation background technique, OH_{wave}. This is illustrated best by the slopes of the overall measurement intercomparison plots (Figures 10, 12, and 14), which ranged from 1.05–1.16, well within the instrumental uncertainty of ~26% at 2σ.

With respect to previous studies during which OH has been measured by a LIF instrument equipped with a scavenger injector, the significance of interferences during the campaigns that feature in this work are amongst the lowest observed (Table 4). This can likely be attributed to two main factors: environment and instrumental. In terms of the former, none of the studies described in the present study took place in forested environments, where the most significant interferences have been observed (Mao et al., 2012; Novelli et al., 2014a; Feiner et al., 2016). However, as mentioned previously, the AIRPRO summer campaign did share
610 some characteristics, in that high BVOC and low NO mixing ratios were observed in the afternoon. Despite



this, OHwave and OHchem were in good agreement. These findings provide confidence in previous measurements of OH using the same instrument, particularly those in a forested region (Whalley et al., 2011), and support the hypothesis that there are unknown OH sources in this type of environment.

The insignificance of daytime interferences during the AIRPRO campaigns are consistent with results of another urban study, CalNex-LA (Research in California at the Nexus of Air Quality and Climate Change) (Griffith et al., 2016). The O₃/H₂O interference is much higher (up to $\sim 4 \times 10^6$ molecule cm⁻³ OH equivalent during CalNex-LA) in the Indiana University (IU) LIF instrument (Dusanter et al., 2009), such that the daytime contributions of $\sim 33\%$ can be explained entirely by this known interference. However, measurements made at a nearby site during the same study (CalNex-SJV) showed daytime contributions of $\sim 20\%$ (Brune et al., 2016), although this may be related to instrumental differences as discussed below. On average, interferences were not observed in the daytime during ICOZA, but they were observed in other coastal campaigns, namely DOMINO (Diel Oxidants Mechanisms In relation to Nitrogen Oxide) HO_x ($\sim 50\%$) (Novelli et al., 2014a) and CYPHEX (CYprus PHotochemistry EXperiment, $\sim 45\%$) (Mallik et al., 2018), as well as in rural regions, HOPE (Hohenpeißenberg Photochemistry Experiment, 20–40%) (Novelli et al., 2014a). Studies in the North China Plain have revealed small interferences on the order of 0–10% (Tan et al., 2017; Tan et al., 2018), with slightly higher but variable contributions of 0–20% in the Pearl River Delta (Tan et al., 2019).

The second major reason for the differences in contributions between the studies listed in Table 4 is likely instrumental effects. For the campaigns in which the highest OH interferences have been observed (Mao et al., 2012; Novelli et al., 2014b; Feiner et al., 2016), OH measurements were made using the Max Planck Institute (MPI) (Martinez et al., 2010) and PSU (Faloona et al., 2004) LIF instruments. These instruments feature laser-multi-pass detection cells, which give rise to larger detection volumes and increased UV fluence, although this may not be relevant considering that the interference signals did not display any laser power dependence for these instruments. The Leeds instrument also differs in terms of cell geometry, where the HO_x cell is composed of a short (5 cm) turreted inlet on top of a large fluorescence cell (additional ~ 8 cm to laser axis, ~ 13 cm total length, and a cell diameter of 25 cm). In contrast, the MPI and PSU instruments feature flow tube-like inlets (14–17 cm from the pinhole to laser axis) mounted on smaller fluorescence cells, facilitating the interaction of sampled gas with the cell walls, which may promote the generation of internal OH. For the measurements listed in Table 4, the Peking University (PKU) instrument (Tan et al., 2017) is most similar to the Leeds FAGE (i.e., single-pass detection, ~ 10 cm total length from sampling inlet to laser axis), for which similar daytime interferences on the order of ~ 0 –20% were observed.

For the ICOZA campaign, nothing could be inferred about the origin of the OH interference signal when one was observed, as it did not exhibit any characteristic diurnal profile (Figure 11), and showed no obvious dependences on a variety of meteorological and chemical parameters. This finding is in contrast to previous studies in which diel profiles (Mao et al., 2012; Feiner et al., 2016) and dependences (Mao et al., 2012; Feiner et al., 2016; Novelli et al., 2017) of the interference have been observed. The occurrence of large (i.e., $> 1 \times 10^6$ molecule cm⁻³) background OH signals (OH_{int} = OH_{wave} – OH_{chem}) after instrumental problems (e.g.,



power cuts, data not shown) implies that the differences may have been instrumental rather than as a result of a species present in ambient air, although the data at these times did pass all quality control filters and therefore could not be rejected. Nonetheless, any differences are still a concern, regardless of their cause; the IPI system thus serves as an additional check on measurement accuracy and operational stability, and is perhaps most useful for fieldwork sites where power supplies are unreliable, for example in more remote areas.

It is possible that, even though the background OH had a flat diurnal profile in each field campaign, the species responsible for any interference observed were different between day and nighttime periods. Thus, analysis of the day and nighttime data separately, as a function of the same parameters, might reveal more information. Considering the recent identification of NO₃ radicals as an internal OH source in LIF instruments (Fuchs et al., 2016), and that OH concentrations have often been underpredicted at night (Faloona et al., 2001; Mao et al., 2012; Ren et al., 2013; Hens et al., 2014; Lu et al., 2014; Tan et al., 2017), this is perhaps the most interesting period for further study. However, for the data presented in this work, robust quantitative nighttime analyses are not possible due to OH measurements being below or close to the instrument LOD.

In this work, there are several key findings that stand out. First, OHwave and OHchem were in good agreement even at the very low NO concentrations of < 100 pptv during ICOZA, and the moderate afternoon levels (~500 pptv on average but often < 100 pptv (Shi et al., 2018)) during the AIRPRO summer campaign. While the role of isoprene could not be assessed for ICOZA, due to the limited range of concentrations observed (< 0.2 ppbv), it reached high levels during AIRPRO summer (up to 7.9 ppbv, larger than seen in some forested regions) but did not seem to perturb the agreement between the two measurements. In addition, very high levels of aromatic VOCs were observed during both AIRPRO winter and summer, where the agreement between OHwave and OHchem suggests that the intermediates of aromatic oxidation, such as exotic bicyclic species (Birdsall et al., 2010) and highly-oxygenated molecules (HOMs) (Wang et al., 2017; Molteni et al., 2018; Hammes et al., 2019), do not give rise to OH interferences, which is postulated to be the case for intermediates (SCIs) in the ozone-oxidation of alkenes (Novelli et al., 2014b; Novelli et al., 2017; Rickly and Stevens, 2018). However, the large alkene and ozone concentrations observed during AIRPRO summer should favour the formation of these SCIs, but significant interferences were not observed, consistent with laboratory investigations of the isoprene interference and casting doubt on the SCI hypothesis. Although, the AIRPRO SCI concentrations also depend on the magnitude of the SCI loss rates, which could be high if elevated levels of SO₂ (Welz et al., 2012; Sheps et al., 2014) or organic acids (Welz et al., 2014) were present.

Considering the success of the first three field deployments of the IPI system, and given that it does not reduce the instrument sensitivity towards OH, it is suggested that the system is adopted for permanent use in ambient studies, although conventional sampling should still be performed from time-to-time to check for potential artefacts caused by the IPI system itself. Another advantage of the IPI system is that it reduces the amount of solar light entering the pinhole, which reduces the size and variability of daytime background signals and therefore improves signal-to-noise and hence detection limits. It is recommended that the IPI propane concentration is kept the same as the summer AIRPRO campaign, as it is possible that the slightly



685 poorer agreement between OHwave and OHchem during ICOZA was because of the lower propane flow
used (i.e., the flow was not sufficient to ensure that OH generated from all steady-state sources was removed),
although this cannot be verified.

690 Future field campaigns using the IPI will allow for the assessment of interferences in the Leeds FAGE
instrument for a range of different environments. From these, the contribution of interferences for previous
studies in similar environments, where measurements were made prior to the discovery of significant
interferences in the LIF measurement of OH reported by others, may be inferred. The measurement-model
comparisons may then be reassessed in light of any new information regarding the accuracy of OH
measurements. Regardless of the reasons for any differences between the two measures of OH (i.e., chemical
interferences or instrumental problems such as during recovery periods after power cuts), the IPI system
695 serves as an additional check on OH observations, increasing confidence in the validity of the data obtained.

5 Conclusions

The addition of an IPI system to the Leeds ground-based FAGE instrument allowed for a comprehensive
investigation of OH measurement interferences in both the laboratory and the field. Following its
optimisation and thorough characterisation in terms of sensitivity and external and internal OH removal
700 efficiency, laboratory experiments were conducted to assess potential interferences from (1) the photolysis
of O₃ in the presence of H₂O vapour, (2) the intermediates and products of isoprene ozonolysis, and (3) NO₃
radicals. For O₃ + H₂O, a small but potentially significant interference (at high O₃ levels) was found, but
interferences from isoprene ozonolysis products and NO₃ radicals were shown to be insignificant under
typical atmospheric conditions.

705 Field campaigns conducted in the UK and China showed that, on average, the Leeds ground-based FAGE
instrument does not suffer from significant interferences in the detection of OH. It was only under the very
high OH levels of $> 1.5 \times 10^7$ molecule cm⁻³ sometimes observed during the AIRPRO summer campaign
that interferences were found consistently, although their contributions (~15–20%) were smaller than the
instrumental accuracy of 26% at 2σ. Large interference signals ($> 1 \times 10^6$ molecule cm⁻³) were occasionally
710 observed during the ICOZA campaign, but always after instrumental problems such as power cuts, suggesting
that the OHchem method serves as an additional tool for verifying instrument stability and validating
measurements. The Leeds IPI system will find continued use in future fieldwork.

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Tables

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Table 1. Overall meteorological and chemical conditions encountered during each field campaign, including example VOCs. Values are given as the median of all points that coincide with IPI sampling periods, except for $J(\text{O}^1\text{D})$ and O_3 , which are reported as diurnally-averaged maxima.

	ICOZA	AIRPRO winter	AIRPRO summer
<i>Dates (IPI sampling)</i>	3–8 and 12–16 Jul, 2015	2–7 Dec, 2016	23 May–25 Jun, 2017
<i>Location</i>	52°57'02''N, 1°07'19''E	39°58'28''N, 116°22'16''E	
<i>Meteorological</i>			
Temperature (°C)	16	6.1	26
H ₂ O (%)	1.5	0.4	1.6
Wind speed (ms ⁻¹)	5.8	0.9	0.4
$J(\text{O}^1\text{D})$ (10 ⁻⁶ s ⁻¹)	16	3.5	19
<i>Chemical</i>			
O ₃ (ppbv)	42	15	90
NO (ppbv)	0.19	22	0.81
NO ₂ (ppbv)	2.2	33	17
CO (ppbv)	100	1120	460
Propane (ppbv)	0.26	6.2	3.8
Isoprene (ppbv)	0.02	0.07	0.38
Benzene (ppbv)	0.03	1.4	0.46
k'_{OH} (s ⁻¹)	4.4	38	25

^aIntegrated Chemistry of OZone in the Atmosphere

^ban integrated study of AIR pollution PROcesses in Beijing (Shi et al., 2019)

1045



Table 2. Internal removal of OH ($\%$, $\pm 2\sigma$) as a function of propane mixing ratio in the IPI flow tube, determined as shown in Figure 6 (see text for details).

Propane (ppmv)	Experiment no.	Internal removal (%)
110 (used for ICOZA and AIRPRO winter)	1	-0.1 ± 4.8
	2	0.3 ± 7.7
	3	-0.9 ± 16
	<i>Average $\pm 2 SD$</i>	-0.2 ± 1.1
550	1	1.0 ± 9.6
1100 (used for AIRPRO summer)	1	1.9 ± 12
	2	4.2 ± 11
	3	2.5 ± 11
	<i>Average $\pm 2 SD$</i>	2.8 ± 2.3

1050

Table 3. Summary of interference tests with O_3 and isoprene (ISO) in the presence of propane (PROP), based on the data in Figure 8.

Test	O_3 (ppmv)	H_2O (%)	ISO (ppmv)	PROP (ppmv)	OHint (molecule cm^{-3})				
					Obs. <i>corr.</i>	^a O_3/H_2O	^b OP3 <i>levels</i>	^c AIRPRO <i>levels</i>	2017
A	1.64	0.73	0	110	1.0 $\times 10^7$	0	N/A	N/A	
B	1.86	0.07	16	110	1.9 $\times 10^7$	1.8×10^7	21	430	
C	1.83	0.98	16	110	1.6 $\times 10^7$	8.0×10^5	1	19	
D	1.85	0.07	16	1100	1.4 $\times 10^7$	1.3×10^7	15	310	

^aCorrected using equation (E7)

^bOxidant and Particle photochemical processes field campaign in Borneo, 2008: average $O_3 = 10$ ppbv, ISO = 3.5 ppbv

^cDiurnally-averaged maximum $O_3 = 90$ ppbv, overall maximum ISO = 7.9 ppbv

1055



Table 4. Average contributions of FAGE background signals to the total OH measured (= (OH_{wave} – OH_{chem})/OH_{wave}) during ambient air studies where a chemical modulation technique was employed.

Study	Year	Location	Environment Type	Contribution (%)		Reference(s)
				Daytime	Nighttime	
PROPHET	1998	N Michigan	Forest, isoprene dominated	Not tested	~0	Faloona et al (2001)
BEARPEX	2009	NE California	Forest, ^a MBO dominated	40–60	50	Mao et al (2012)
CABINEX	2009	N Michigan	Forest, isoprene dominated	Not tested	50–100	Griffith et al (2013)
SHARP	2009	Houston, Texas	Urban	30	50	Ren et al (2013)
CalNex-LA	2010	Pasadena, California	Urban, downwind of LA	33*	Not reported	Griffith et al (2016)
CalNex-SJV	2010	Bakersfield, California	Urban	20	80	Brune et al (2016)
DOMINO	2010	El Arenosillo, near Huelva, SW Spain	Coastal, close to petrochemical industry	50	100	Novelli et al (2014)
HO _x						
HUMPPA-COPEC	2010	Hyytiälä, SW Finland	Boreal forest, terpene dominated	60–80	100	Hens et al (2014); Novelli et al (2014); Novelli et al (2017)
HOPE	2012	Hohenpeissenberg, S Germany	Rural	20–40	100	Novelli et al (2014); Novelli et al (2017)
SOAS	2013	near Brent, Alabama	Forest, isoprene dominated	80	>70	Feiner et al (2016)
Wangdu	2014	North China Plain	Rural, urban influenced	10	Not reported	Fuchs et al (2017); Tan et al (2017)
CYPHEX	2014	NW Cyprus	Coastal, influenced by processed European emissions	45	100	Mallik et al (2018)
PRIDE-PRD2014	2014	Pearl River Delta	Suburban, 60 km SW of Guangzhou	0–20	0–20	Tan et al (2019)
BEST-ONE	2016	North China Plain	Suburban, 60 km NE of Beijing	~0	~0	Tan et al (2018)
ICOZA	2015	N Norfolk Coast, UK	Coastal, London outflow	~0	~0	This work
AIRPRO	2016	Beijing, China	Urban	~0	Nighttime OH almost always < LOD	This work
Winter						
AIRPRO	2017	Beijing, China	Urban	~0	~0	This work
Summer						

^aMBO = 2-methyl-3-buten-2-ol, a biogenic volatile organic compound



Figures

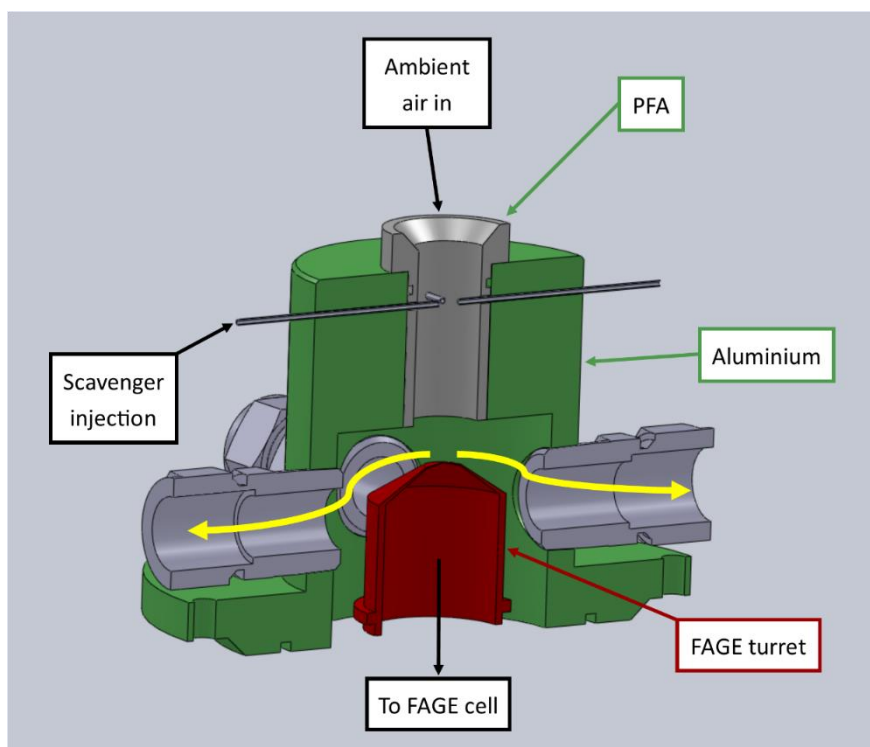


Figure 1. Labelled SolidWorks model of the Leeds inlet pre-injector (IPI). The scavenger is injected into the centre of the perfluoroalkoxy (PFA) flow tube via four 0.25 mm ID needles. The thick yellow arrows indicate the direction of the sheath flow.

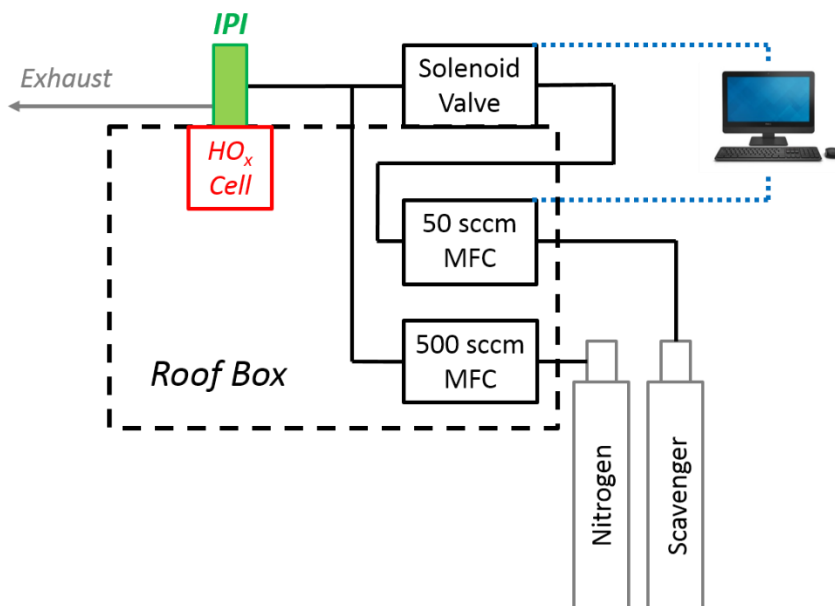


Figure 2. Diagram of the gas flows involved in IPI scavenger injection (not to scale). The two mass flow controllers (MFCs) are housed in the roof box, where the scavenger MFC (0–50 sccm) and injection valve (in a weatherproof housing on top of the roof box) are controlled using the main FAGE PC situated in the container laboratory.

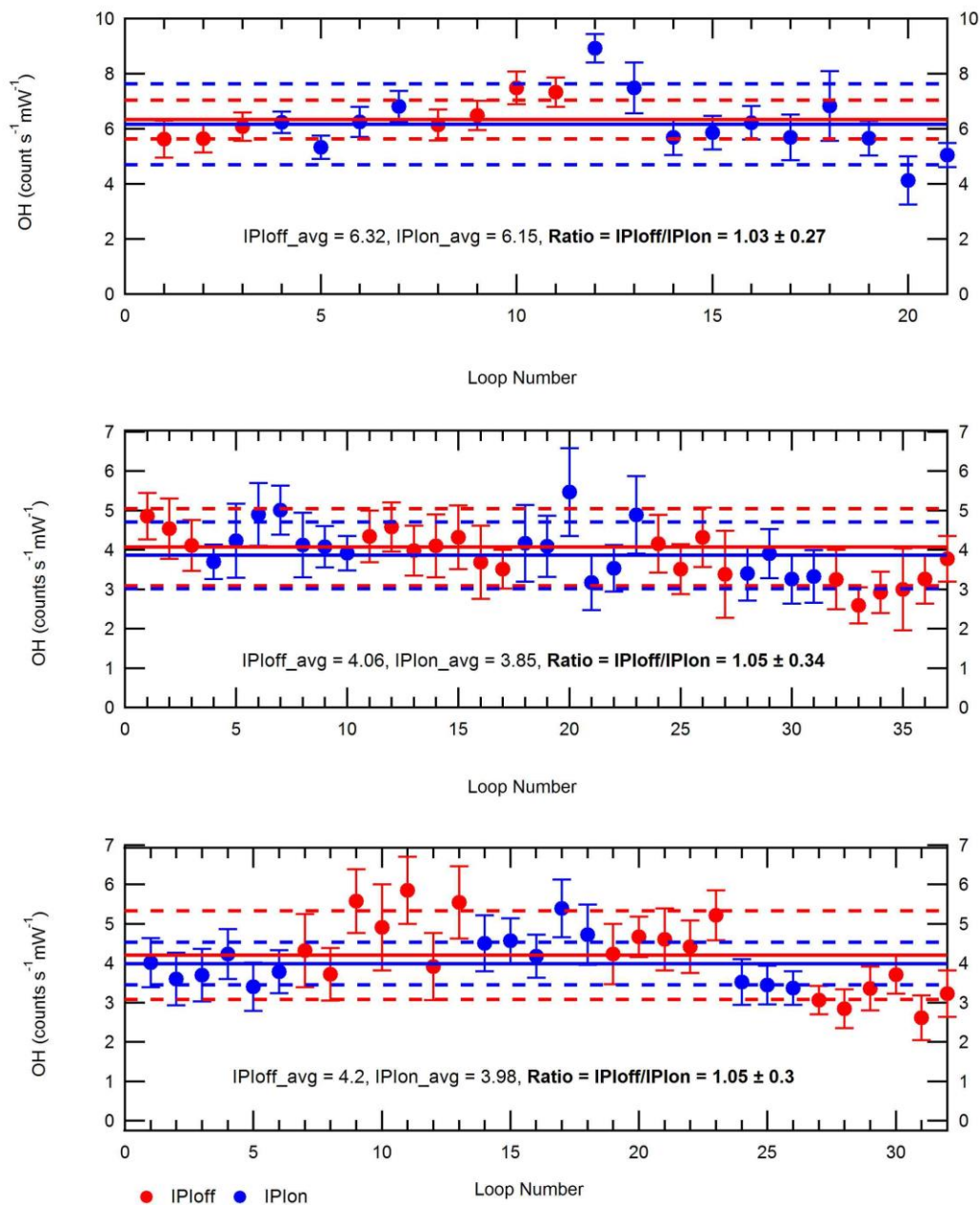


Figure 3. Testing of OH losses in the IPI system. Each panel shows repeat measurements of OH signals ($\pm 2\sigma$) over the course of one day, where high OH concentrations were generated using a 184.9 nm Hg lamp placed near the instrument inlet. Blue and red markers denote individual measurements (one measurement “loop”, i.e., one wavelength online–offline cycle) performed with (“IPIon”) and without (“IPIoff”) the IPI system, respectively. Solid lines correspond to the average signals for each day, with 2σ standard deviations (SD) shown by the dashed lines.

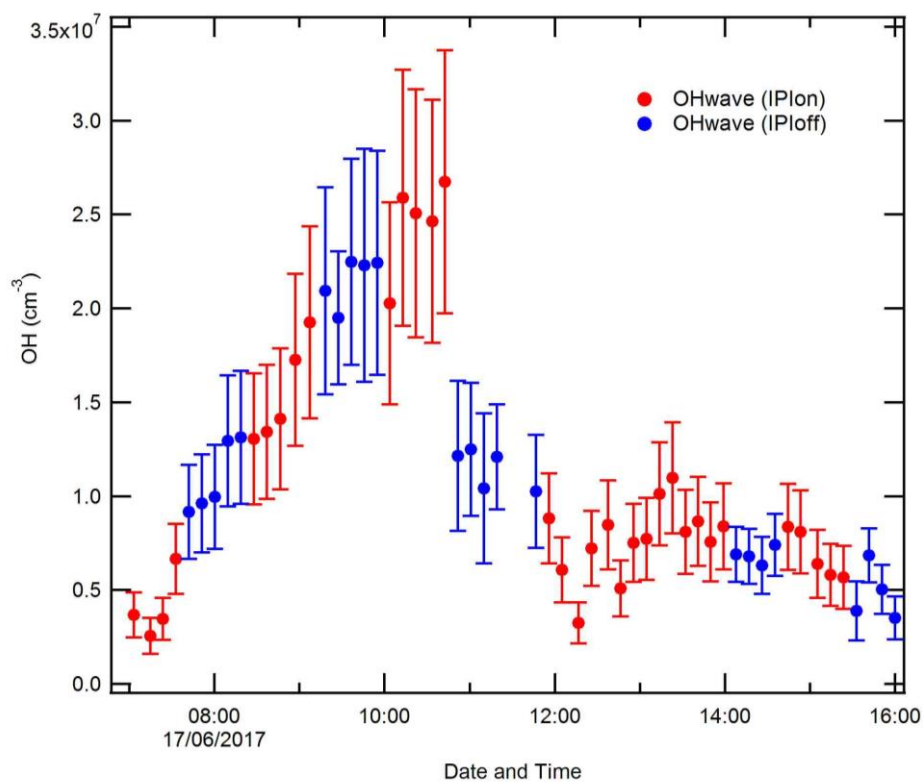


Figure 4. Time series of OHwave concentrations in Beijing on 17th June 2017, a period of high OH levels in the summer 2017 AIRPRO (an integrated study of AIR pollution PROCesses in Beijing) campaign. Blue and red markers ($\pm 2\sigma$) denote observations made with and without the IPI system, respectively.

5

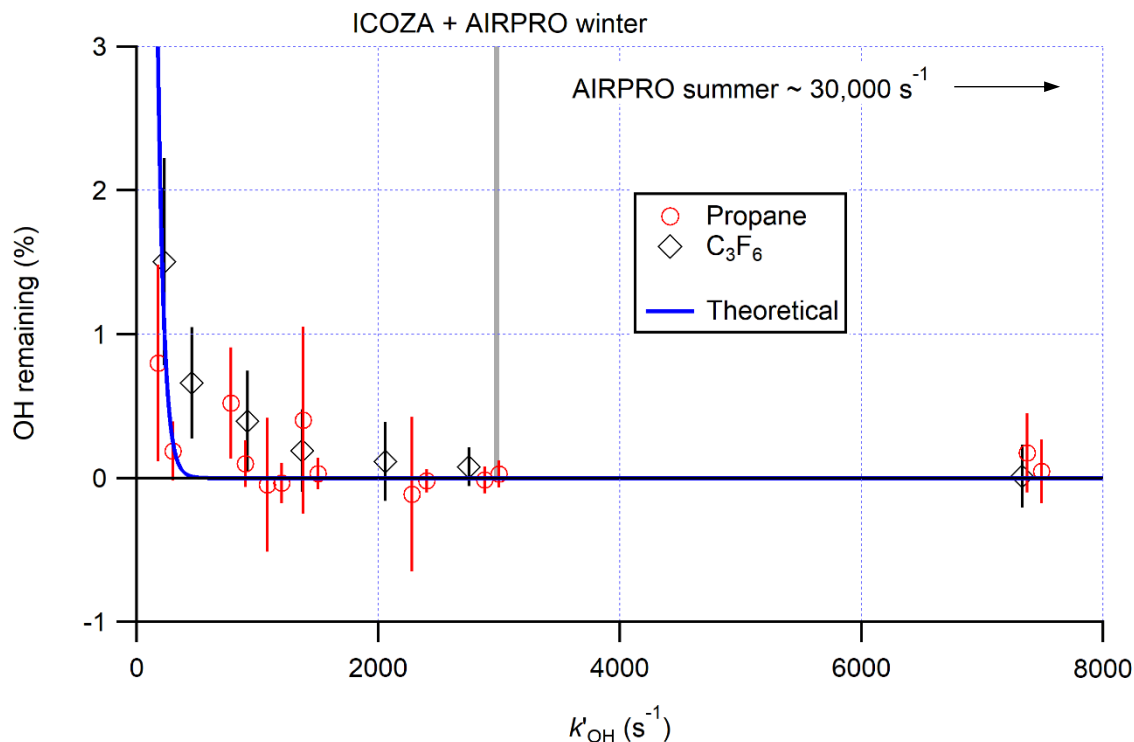


Figure 5. Proportion of the OH signal remaining (i.e., external OH removal efficiency) after addition of increasing concentrations of propane and perfluoropropene (C_3F_6) scavengers to the IPI flow tube, converted to equivalent OH reactivities (k'_{OH}) to account for the different rate constants for the reaction of each scavenger with OH. Error bars denote the 2σ SD of repeat experiments. The blue curve corresponds to the theoretical scavenging efficiency assuming perfect mixing, using the estimated residence time, $\tau \sim 20$ ms. The propane OH reactivity used for the ICOZA (Integrated Chemistry of OZone in the Atmosphere) and AIRPRO winter campaigns is given, but that used for AIRPRO summer is off-scale.

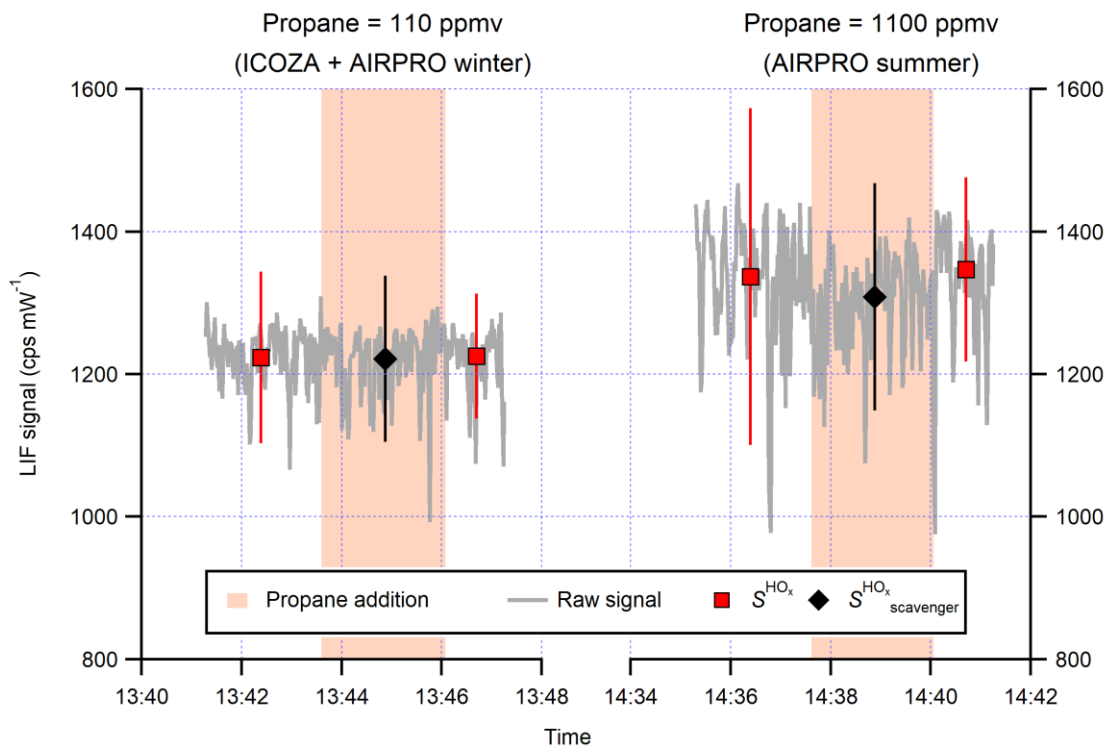


Figure 6. Time series of the LIF signal during internal OH removal experiments. The raw 1 s data are given by the grey line. NO was continuously added to the FAGE cell during these experiments, and points where propane was added to the IPI flow tube are indicated by the orange shaded panels, with the corresponding signal averages ($\pm 2\sigma$) shown as markers (see text for details). The first experiment (left-hand side) corresponds to the propane mixing ratio used for ICOZA, while the second (right-hand side) corresponds to that used for AIRPRO. The results of the internal OH removal experiments are summarised in Table 2.

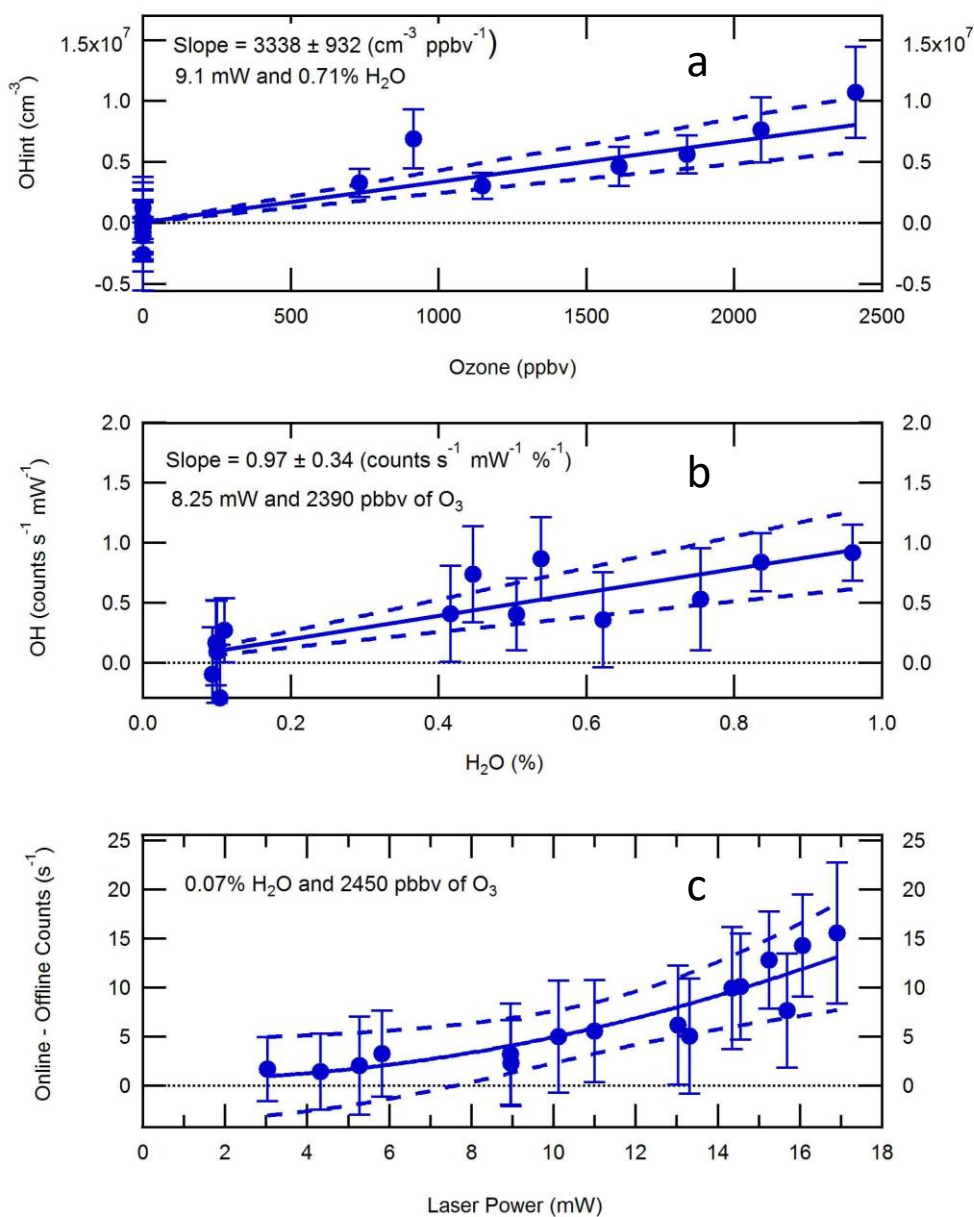


Figure 7. OH interference ($\pm 2\sigma$) from $\text{O}_3 + \text{H}_2\text{O}$ as a function of (a) O_3 , (b) H_2O , and (c) laser power. The interference signal is linear in O_3 and H_2O mixing ratios and quadratic in laser power, confirming the two-photon nature of the process. Normalising the slope in panel (a) to $\text{O}_3 = 1$ ppbv, $\text{H}_2\text{O} = 1\%$, and laser power = 1 mW yields an OH interference equivalent to a concentration of 520 ± 140 molecule cm^{-3} .

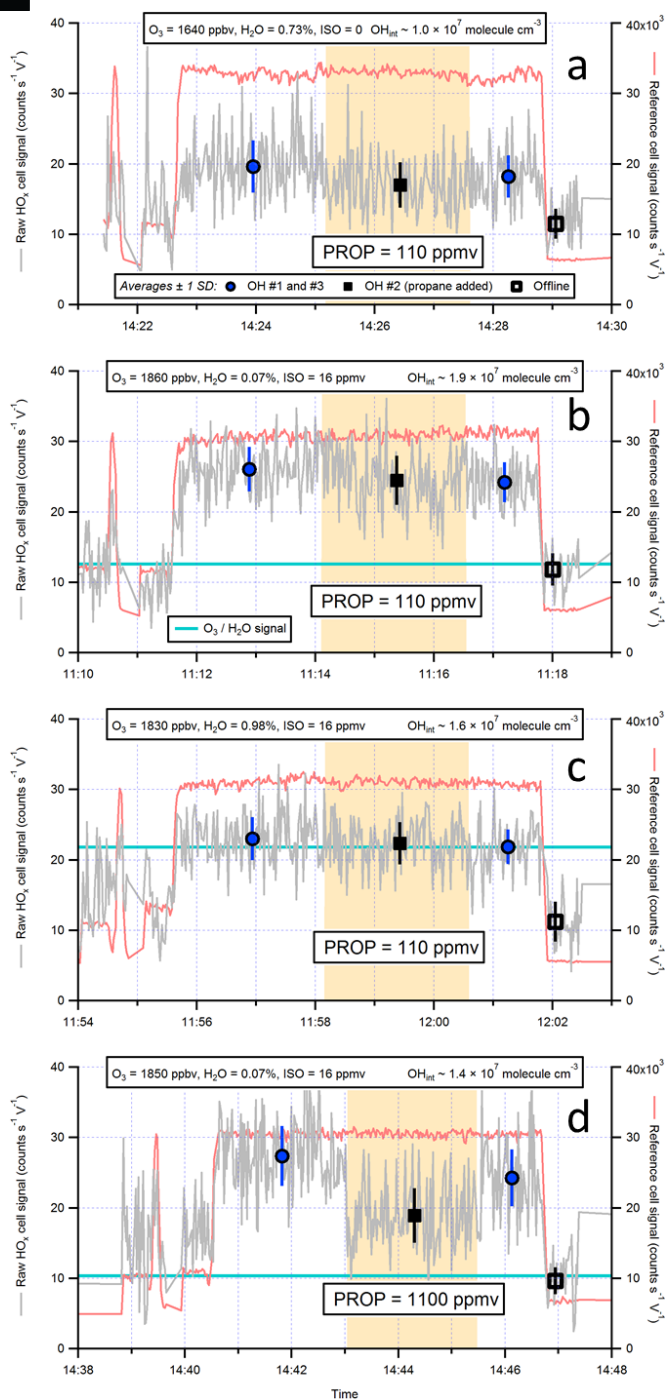


Figure 8. Isoprene (ISO) ozonolysis interference tests: (a) O₃/H₂O only, (b) O₃ and ISO under dry conditions, (c) O₃ and isoprene with H₂O added, and (d) O₃ and isoprene under dry conditions, but with a higher concentration of propane (PROP) to remove any steady-state generated OH. Shaded areas are periods of propane addition, and the light blue lines correspond to the calculated signals from O₃ + H₂O only (for experiments with isoprene present). The interference signals (“OH #2” – “offline”) were used to derive equivalent OH concentrations (OH_{int}), which are on the order of ~1–2 × 10⁷ molecule cm⁻³. These experiments are summarised in Table 3. See text for further details.

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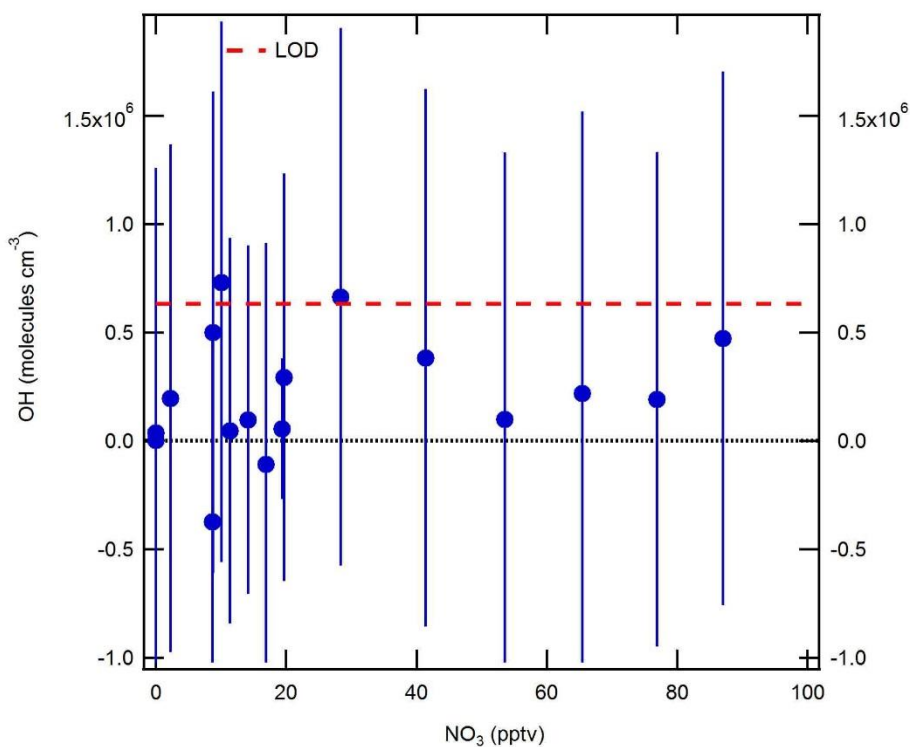


Figure 9. Equivalent OH concentrations ($\pm 2\sigma$) measured during NO₃ radical interference tests. NO₃ concentrations were calculated using a box model and OH interference signals were corrected for the interference from O₃ + H₂O. The OH limit of detection (LOD, 6.3×10^5 molecule cm⁻³, SNR = 2) is denoted by the red dashed line.

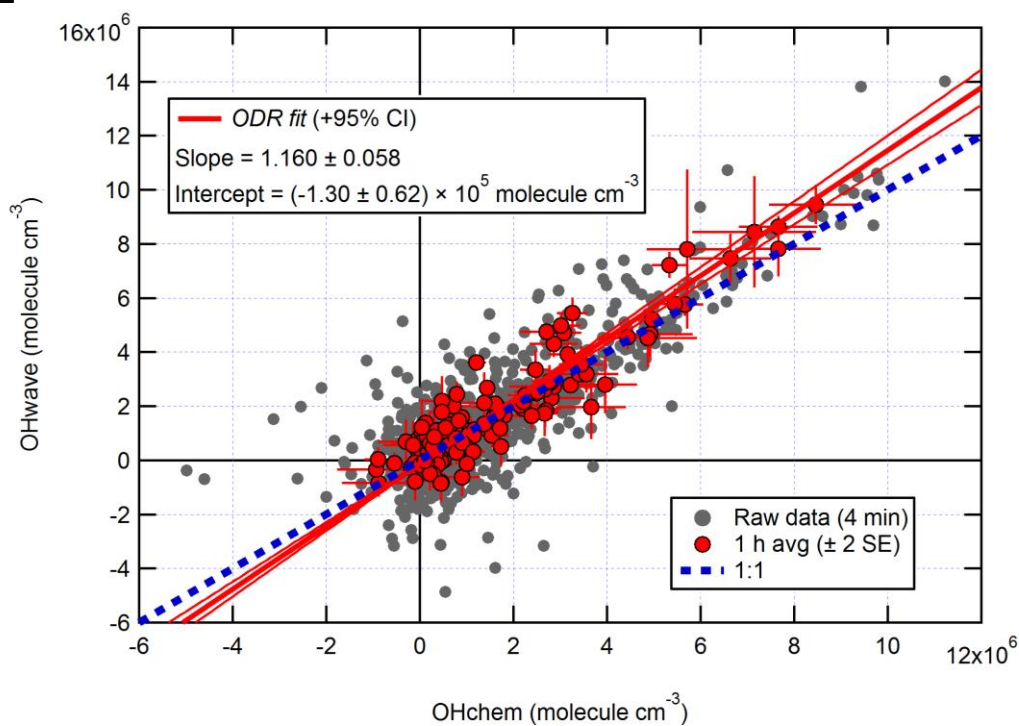


Figure 10. Overall intercomparison of OHwave and OHchem observations from the ICOZA campaign. Grey markers represent raw data (4 min), with 1 h averages (± 2 standard errors (SE)) in red. The thick red line is the orthogonal distance regression (ODR) fit to the hourly data, with its 95% confidence interval (CI) bands given by the thin red lines; fit errors given at the 2σ level. For comparison, 1:1 agreement is denoted by the blue dashed line. OHwave data were corrected for the known interference from $O_3 + H_2O$.

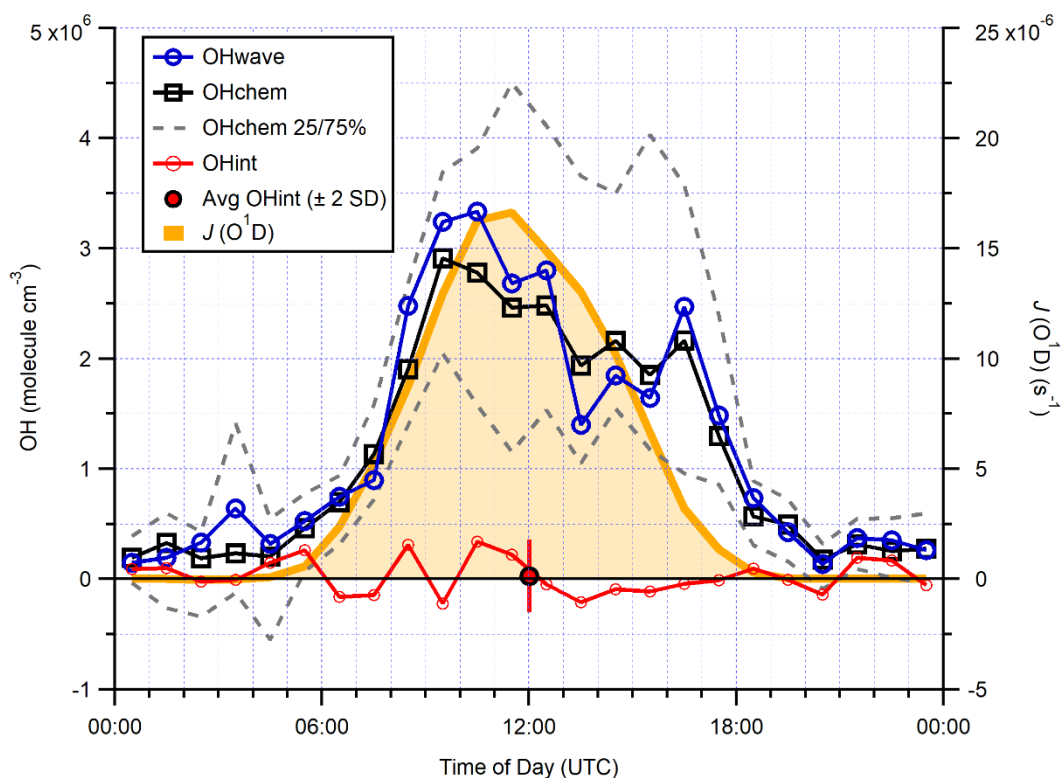


Figure 11. Hourly median diurnal profiles of OHwave, OHchem, and $J(O^1D)$ (right axis) from the ICOZA campaign. Also shown (red line and markers) is the hourly median diurnal profile of OHint (= OHwave – OHchem), calculated from individual 4 min data points; the single red marker corresponds to the average ($\pm 2\sigma$) of this trace. The variability (interquartile range, IQR) in OHchem measurements is denoted by the grey dashed lines, not shown for others for clarity. OHwave data were corrected for the known interference from $O_3 + H_2O$.

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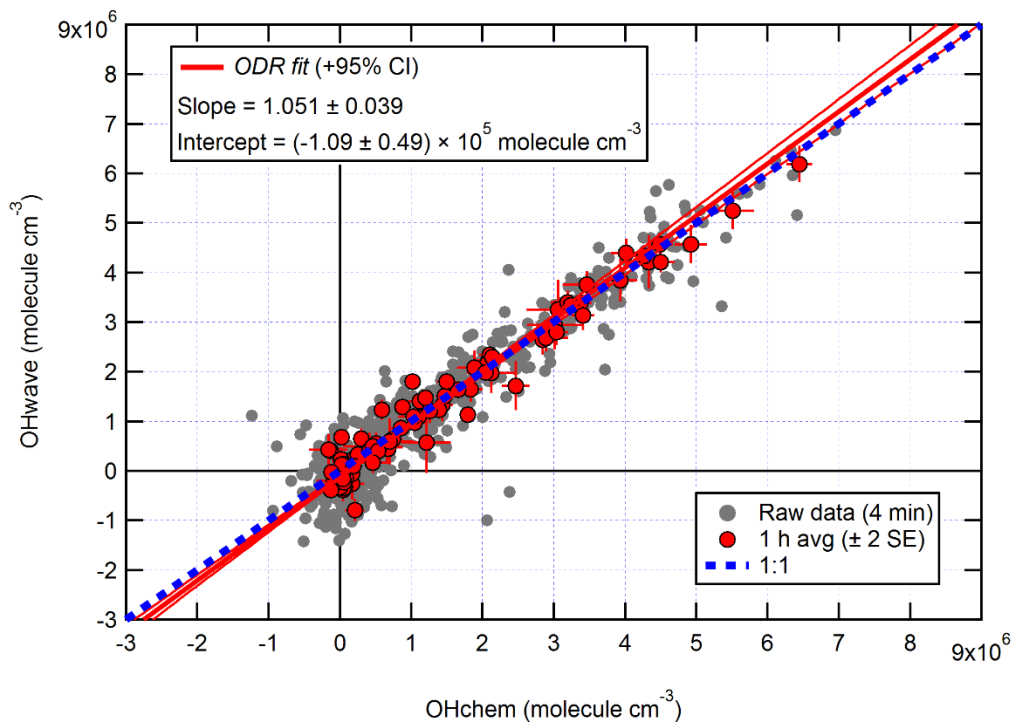


Figure 12. Overall intercomparison of OHwave and OHchem observations from the winter 2016 AIRPRO campaign. Grey markers represent raw data (4 min), with 1 h averages (± 2 SE) in red. The thick red line is the ODR fit to the hourly data, with its 95% CI bands given by the thin red lines; fit errors given at the 2σ level. For comparison, 1:1 agreement is denoted by the blue dashed line. OHwave data were corrected for the known interference from $\text{O}_3 + \text{H}_2\text{O}$.

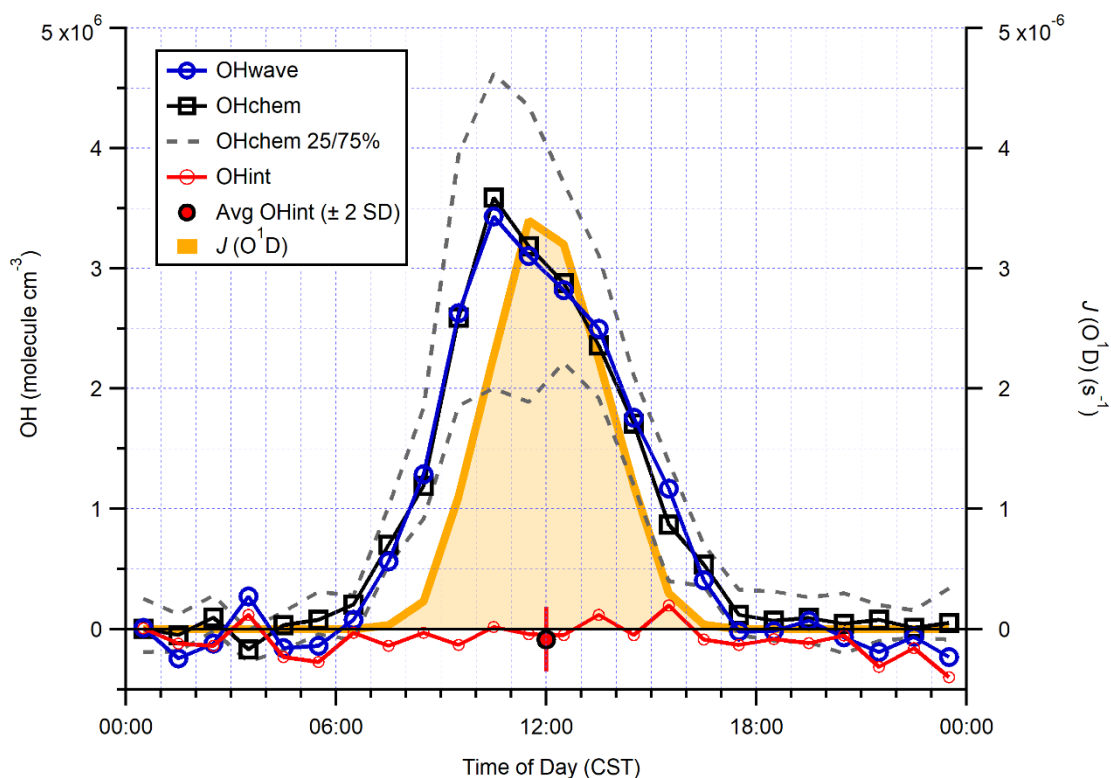


Figure 13. Hourly median diurnal profiles of OHwave, OHchem, and $J(O^1D)$ (right axis) from the winter 2016 AIRPRO campaign. Also shown (red line and markers) is the hourly median diurnal profile of OHint, calculated from individual 4 min data points; the single red marker corresponds to the average ($\pm 2\sigma$) of this trace. The variability (IQR) in OHchem measurements is denoted by the grey dashed lines, not shown for others for clarity. OHwave data were corrected for the known interference from $O_3 + H_2O$.

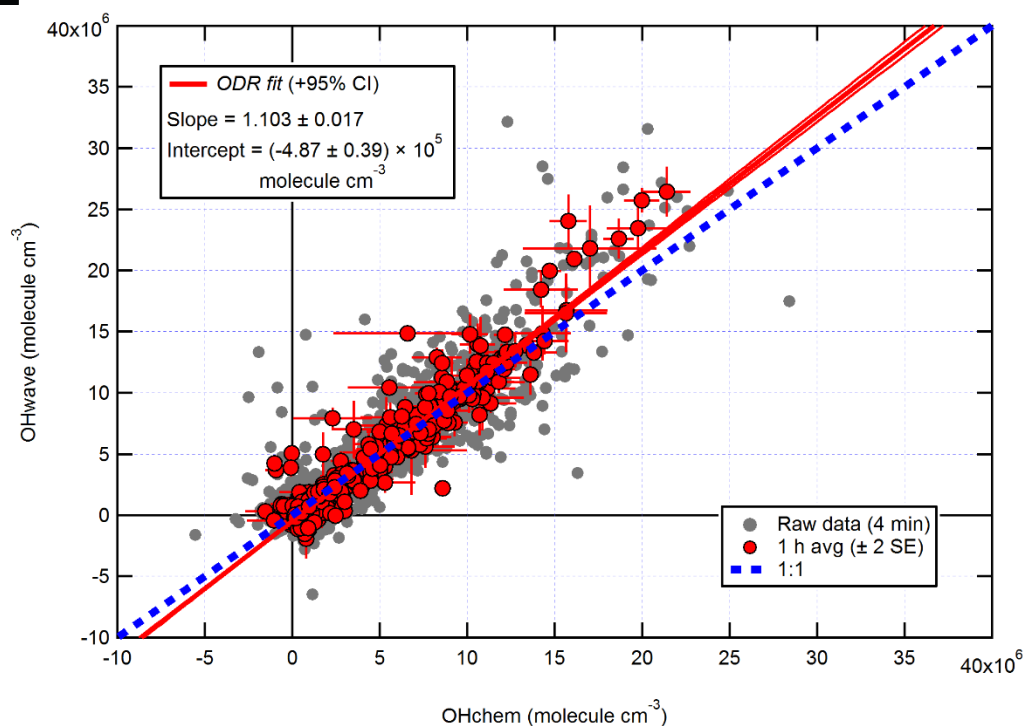


Figure 14. Overall intercomparison of OHwave and OHchem observations from the summer 2017 AIRPRO campaign. Grey markers represent raw data (4 min), with 1 h averages (± 2 SE) in red. The thick red line is the ODR fit to the hourly data, with its 95% CI bands given by the thin red lines; fit errors given at the 2σ level. For comparison, 1:1 agreement is denoted by the blue dashed line. OHwave data were corrected for the known interference from $O_3 + H_2O$.

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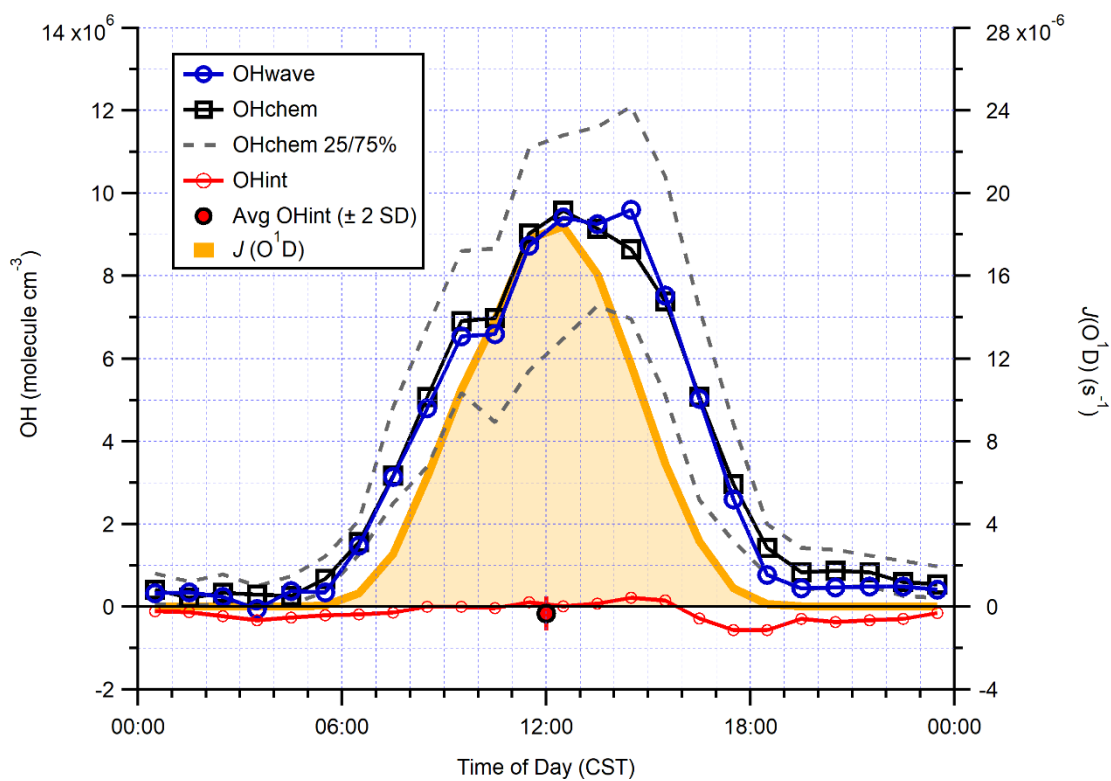


Figure 15. Hourly median diurnal profiles of OHwave, OHchem, and $J(O^1D)$ (right axis) from the summer 2017 AIRPRO campaign. Also shown (red line and markers) is the hourly median diurnal profile of OHint, calculated from individual 4 min data points; the single red marker corresponds to the average ($\pm 2\sigma$) of this trace. The variability (IQR) in OHchem measurements is denoted by the grey dashed lines, not shown for others for clarity. OHwave data were corrected for the known interference from $O_3 + H_2O$.

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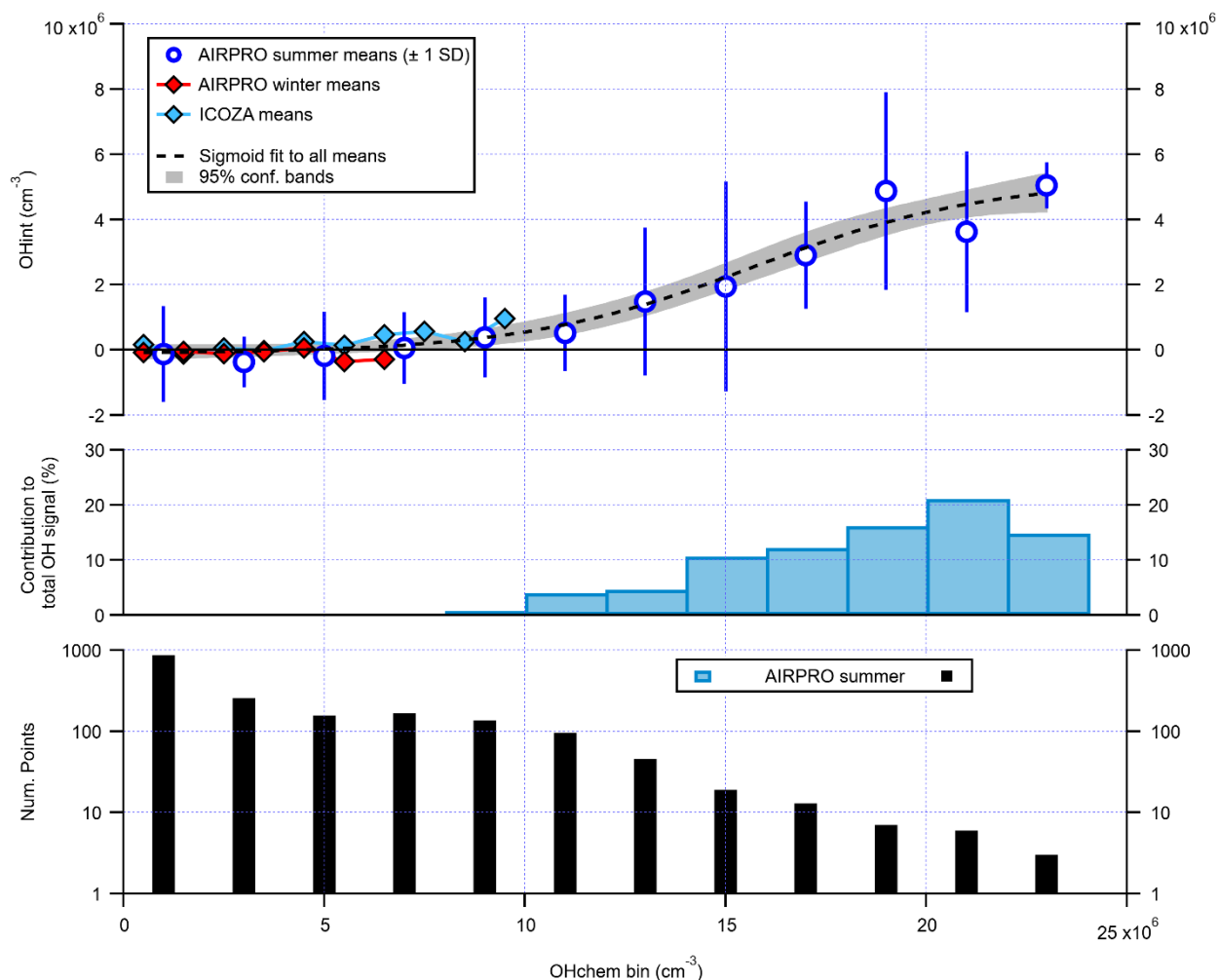


Figure 16. Relationship between OHint and OHchem using binned data. The error bars for AIRPRO summer (upper panel, blue markers) denote 1 SD, not shown for AIRPRO winter and ICOZA for clarity. The black dashed line corresponds to a sigmoid fit used to guide the eye only. The contribution of interferences to the total OHwave signal (= OHint/OHwave × 100%) for the AIRPRO summer campaign is shown in the middle panel, with the number of points in each bin shown in the lower panel. All OHint data used here have been corrected for the known interference from O₃ + H₂O.

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