Long-term field measurements of OH reactivity using laser flash photolysis coupled with time-resolved broadband UV absorption spectroscopy

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1. Introduction

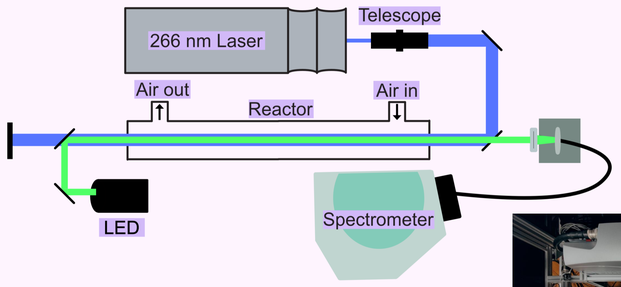
- Volatile organic compounds (**VOCs**), emitted from both anthropogenic and biogenic sources, have complex impacts on air quality and climate
- There is an estimated **100,000 VOCs** found in ambient air, and they cannot all be measured using traditional direct techniques [1]
- **OH reactivity** (k_{OH}) is a pseudo-first order rate coefficient that quantifies the total reactive pollutant loading in an air mass, and can be used to determine the **total impact of VOCs**

$$k_{OH} = k_{CO+OH}[CO] + k_{NO+OH}[NO] + k_{NO_2+OH}[NO_2] + k_{VOC+OH}[VOC] + \cdots = \sum k_{xi}[x]_i$$

- All techniques used by OH reactivity instruments involve producing above ambient OH concentrations and determining the **OH decay kinetics**
- Current instruments designed for measuring OH reactivity are often technically **complex** and **expensive** [2] or unsuitable for use in urban environments owing to **interferences at high NO** [3]
- In this work, a new instrument based on the **laser flash pump-probe technique** [4][5] is compared to a pump-probe instrument utilising **Laser Induced Fluorescence** (**LIF**) for OH detection, and measurements from the ongoing Birmingham field campaign are presented.

2. The Novel UV Spectroscopy OH Reactivity Instrument

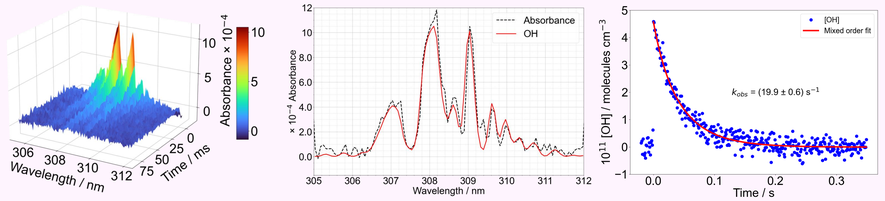
- A novel OH reactivity instrument has been developed utilising broadband time-resolved **UV absorption spectroscopy** as a detection technique
- The instrument produces OH by photolysing O_3 with a **266 nm Nd:YAG laser** in the presence of water vapour
- A **probe beam** at ~308 nm, produced by a UV LED, is aligned through the reactor and the absorption of light monitored by an **integrated spectrometer** and **charge coupled device** camera



$$O_3 \xrightarrow{h\nu} O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow 2OH$$

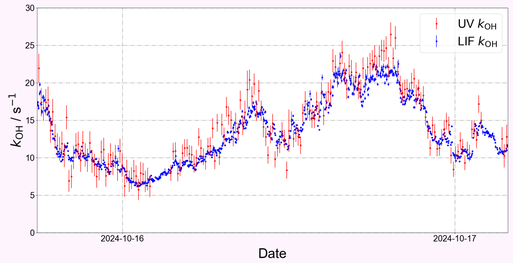
- OH cross-sections [6] are then fitted to the **absorbance spectra** to determine OH concentrations using the Beer-Lambert law

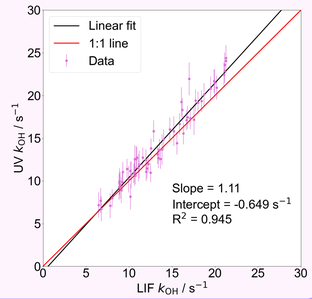


- The instrument has a **[OH] LOD** of **5×10^{10}** molecule cm^{-3} and a k_{OH} **LOD** of **1 s^{-1}**, with an averaging time of 600 s

3. Leeds Intercomparison

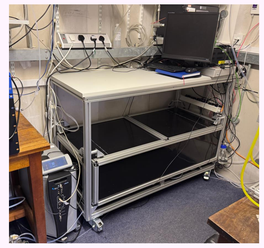
- The new UV instrument was compared to another pump-probe instrument that uses **LIF spectroscopy** [5]
- The LIF instrument has previously undergone rigorous **testing** and **intercomparison** against other k_{OH} field instruments [3]
- Both instruments sampled ambient air from the same courtyard at the University of Leeds, UK, in October 2024
- This intercomparison showed **excellent agreement**

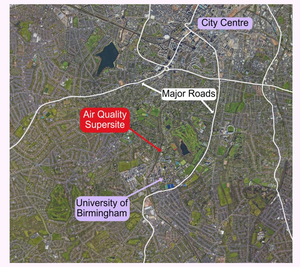




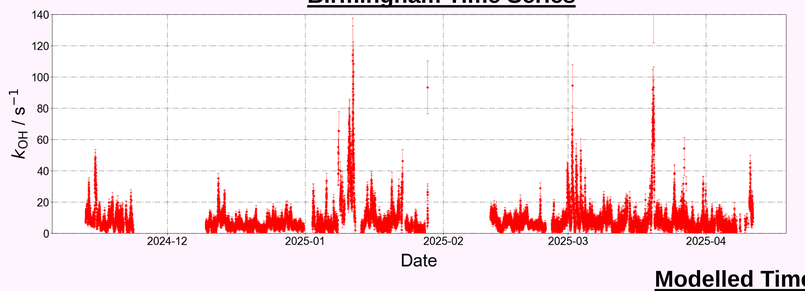
4. Birmingham Reactivity

- The UV instrument has been measuring ambient air at the **Birmingham Air Quality Supersite,** UK, since November 2024. The Supersite contains instruments to measure NO_x, VOCs, CO, O_3 and aerosols alongside meteorological measurements
- Measurements so far have indicated a **mean** reactivity of **8.5 s^{-1}** and a **maximum** reactivity of **145 s^{-1}**
- The diurnal profile shows a **'rush hour'** peak, and another peak later in the day, which is thought to be caused by a **boundary layer drop**
- Wind direction indicates **higher reactivity** from air passing over Birmingham **city centre** and over major roads

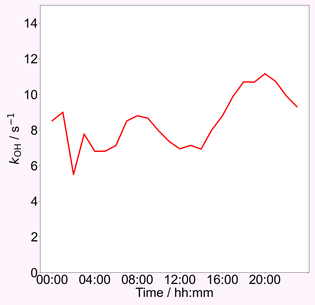




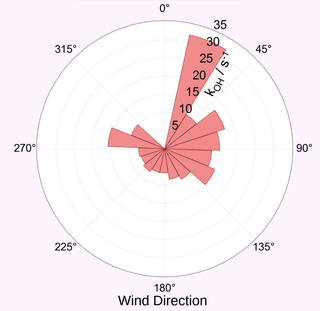
Birmingham Time Series



Diurnal Profile

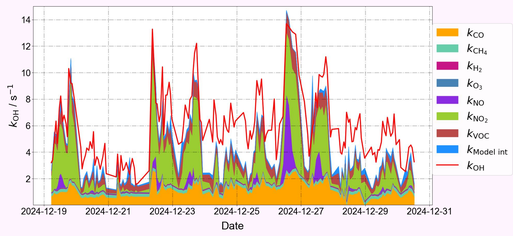


Wind Rose Plot

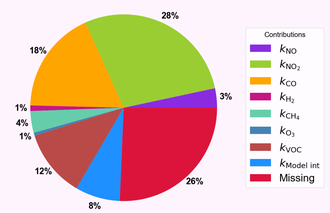


- Box modelling is being conducted using the **Master Chemical Mechanism** and measurements of reactive species from the supersite, with estimated values for CO and CH_4, to determine the **modelled reactivity**
- Initial results indicate that the largest contribution to reactivity arises from **NO_2** (28%) and **CO** (18%), with a **mean** missing reactivity of **26%**

Modelled Time Series



Contributions to Reactivity



5. Conclusions and Further Work

- The **novel UV absorption** spectroscopy OH reactivity instrument **compares well** with a well-characterised LIF spectroscopy pump-probe instrument
- The instrument has been operational at the Birmingham Air Quality Supersite for **over 5 months**
- Measurements at the site will continue in order to determine **seasonal trends** in k_{OH}
- Further work on determining trends in missing reactivity will be conducted using MCM box modelling

References

[1]:Goldstein and Galbally, Environ. Sci. Technol., 41, 1514–1521, 2007
[2]: Williams and Brune, Atmos. Env., 106, 371-372
[3]:Fuchs et al., Atmos. Meas. Tech., 10, 4023-4053 (2017)
[4]:Sadanaga et al., Rev. Sci. Instrum. 75, 2648–2655 (2004)
[5]: Stone et al., Atmos. Meas. Tech., 9, 2827-2844 (2016)
[6]: Dorn et al., J. Geophys. Rs., 100(D4), 7397-7409 (1995)