# Long-term measurements of OH reactivity: A new metric for air quality

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Volatile organic compounds (VOCs) are emitted into the atmosphere from a variety of sources, including vehicle exhausts, industry, agriculture and plants, with estimates of over $10^4$ different VOCs present in ambient air (Goldstein and Galbally, 2007). Once released into the atmosphere the dominant fate for the majority of VOCs is oxidation by hydroxyl (OH) radicals, leading to a complex cascade of reactions, generating secondary pollutants such as ozone ($O_3$) and secondary organic aerosol (SOA), which are harmful to human health.

Poor air quality has been reported as the greatest environmental risk to public health in the UK (DEFRA, 2017), has recently been linked to dementia (Carey *et al*., 2018), and is estimated to cause over 40,000 premature deaths in the UK each year (Royal College of Physicians, 2016). Policies designed to address issues such as air quality and climate rely on accurate knowledge of atmospheric composition, requiring understanding of the emission rates, concentrations, and chemistry of trace VOCs in the atmosphere. However, it is only possible to identify and measure the concentrations of a small fraction of the vast array of VOCs present in the atmosphere (Goldstein and Galbally, 2007), which hinders our ability to provide accurate predictions of air quality and climate. Despite this challenge, it is possible to quantify the presence of unmeasured species, and the extent to which they contribute to the production of ozone and SOA (Yang *et al*., 2016), through measurements of the rate at which OH radicals are consumed in the atmosphere, since almost all species emitted into the atmosphere react with OH (Heard and Pilling, 2003; Stone *et al*., 2012).

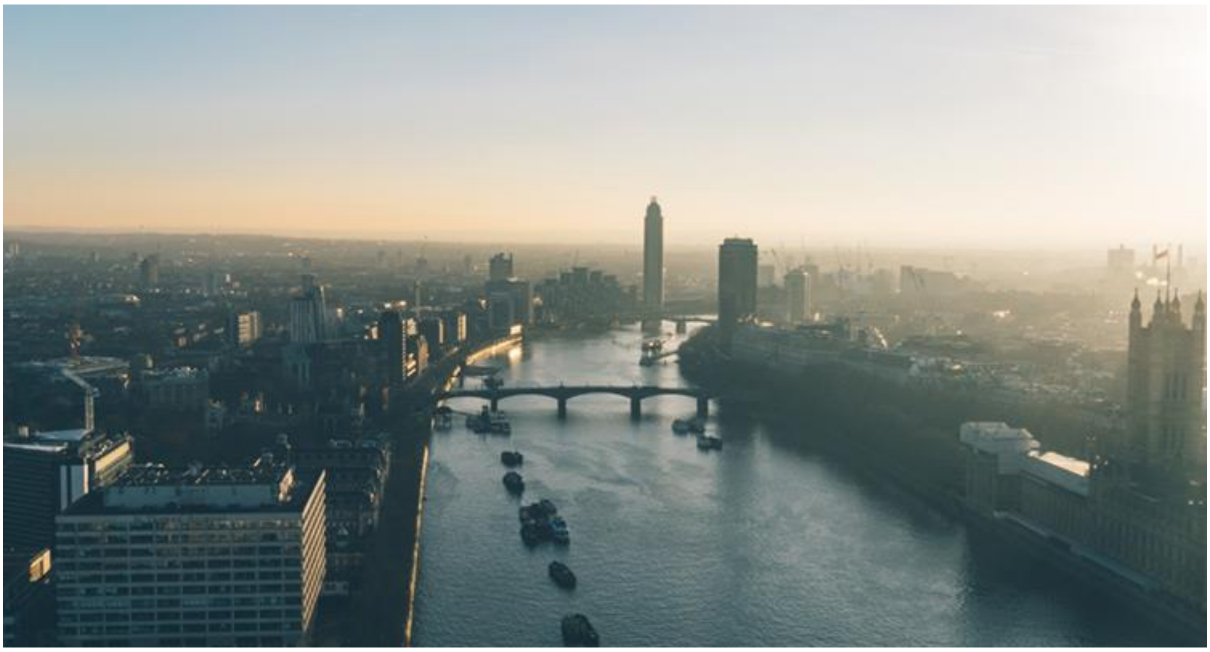

*Figure 1: Air pollution in London, UK. Source: https://nerc.ukri.org/press/releases/2018/02-air/*

Measurements of the total OH loss rate in the atmosphere can be used to define the OH reactivity, which is the pseudo-first-order rate coefficient describing the loss ($k_{OH}$) and the inverse of the chemical lifetime of OH ($\tau_{OH} = 1/k_{OH}$). Comparison between measurements of OH reactivity and calculations based on observations of OH sinks, which include CO, NO, $NO_2$ and VOCs, and laboratory measurements of OH radical kinetics, provides a means to determine the comprehensiveness of the observed sinks (Yang *et al.*, 2016; Fuchs *et al.*, 2017), which enables assessment of the potential contribution of unmeasured species to air quality and climate (Kirchner *et al.*, 2001; Yang *et al.*, 2016).

While several instruments have been developed to measure OH reactivity, including work in the Leeds group which has demonstrated significant impacts of large VOCs ($\geq C_9$) and biogenic emissions in London (Ingham *et al.*, 2009; Stone *et al.*, 2016; Whalley *et al.*, 2016), these instruments tend to be limited to short-term intensive measurements. The capability to make long-term OH reactivity measurements would enhance our abilities to monitor changing trends in pollutant emissions, to assess emissions inventories, and to provide more accurate air quality and climate forecasts. Long term measurements of OH reactivity would provide an exciting new metric for air quality for use by policy makers.

## Objectives:

In this project you will develop a new instrument to enable long-term measurements of OH reactivity in the atmosphere. The instrument will be based on the pump-probe technique (e.g. Sadanaga *et al.*, 2004; Stone *et al.*, 2016), which has been shown to have significant advantages over alternatives such as the flow tube method (Kovacs and Brune, 2001) or the comparative reactivity method (Sinha *et al.*, 2008), particularly in urban or polluted environments (Fuchs *et al.*, 2017). Current instruments used to measure OH reactivity which employ the pump-probe technique use laser flash photolysis of ozone in the presence of water vapour to produce OH radicals (R1-R2), and typically monitor OH radicals using laser-induced fluorescence (LIF) spectroscopy to determine the OH reactivity from the observed loss rate of OH through subsequent reactions with trace species in the atmosphere (R3):

$$O_3 + h\nu\ (\lambda=266\ \text{nm}) \rightarrow O(^1D) + O_2 \qquad \text{(R1)}$$

$$O(^1D) + H_2O \rightarrow 2\ OH \qquad \text{(R2)}$$

$$OH + X \rightarrow \text{loss} \qquad \text{(R3)}$$

where X is any species which reacts with OH. The OH reactivity is thus given by the sum of the products of concentrations of species X and their rate coefficients for reaction with OH ($k_{OH} = \Sigma k_x[X]$). The Leeds OH reactivity instrument has been deployed in a number of field campaigns, in environments including tropical rainforests, coastal marine regions and the the heavily polluted mega-city of Beijing.

This work will reduce the complexity of current OH reactivity instruments using the pump-probe technique by developing a system using a resonance lamp to detect the OH radicals in place of the laser-induced fluorescence system, thereby reducing the complexity and size of the instrument to provide the potential for long-term measurements. Resonance lamps have been shown to display the required sensitivity and selectivity for OH in laboratory experiments (e.g. Crowley *et al.*, 1996; Carl and Crowley, 2001), but have yet to be employed in field instruments to measure OH reactivity. You will be involved in the initial design and characterisation of the instrument, which will then be compared to the existing Leeds instrument and deployed in the field for testing and long-term measurements. You will use numerical models based on the Master Chemical Mechanism (MCM, Saunders *et al.*, 2003; Jenkin *et al.*, 2003) to interpret and understand the measurements, and to determine impacts on air quality and climate. Depending on your interests you may also be involved in laboratory experiments to determine OH radical reaction kinetics using the techniques developed in this project.

## Potential for high impact outcome

The role of chemistry in controlling atmospheric composition is of fundamental importance to our understanding of air quality and climate change. This work will develop a novel field instrument to enable long-term measurements to improve our understanding of atmospheric composition and chemistry, providing greater constraints on model calculations of global oxidising capacity and production of secondary organic aerosol. It is anticipated that this project will enable the provision of a new metric for air quality which may be of use to policy makers and will generate several papers, with potential for publication in high impact journals.

## Training

The student will work under the supervision of Dr Daniel Stone and Prof Dwayne Heard within the Atmospheric and Planetary Chemistry group in the School of Chemistry at the University of Leeds. You will be supported by a range of supervisions from monthly meetings and group presentations, through to daily informal chats with supervisors. You will work in well-equipped laboratories and be part of an active, thriving and well-funded atmospheric chemistry community. The Leeds group receives funding from the National Centre for Atmospheric Science (NCAS) and is part of the Atmospheric Measurement Facility, and has an internationally leading reputation in atmospheric chemistry for field measurements of atmospheric composition, laboratory studies of chemical kinetics and photochemistry, and the development of numerical models and chemical mechanisms, including the Master Chemical Mechanism (MCM, Saunders *et al.*, 2003; Jenkin *et al.*, 2003). Activities in these three areas are intimately linked and interdependent, providing significant advantages. You will be supported to attend both national and international conferences, and will receive a wide range of training, for example in communication skills, project management, and with other technical aspects (for example LabView and computing). The PhD will provide a wide range of experience in the use of high power lasers, vacuum systems, optics, computer controlled data acquisition systems and methods in numerical modelling. You will also have access to training provided by the National Centre for Atmospheric Science such as the Arran Instrumental Summer School and other courses. The successful PhD student will have access to a broad spectrum of training workshops that include managing your degree and preparing for your viva (http://www.emeskillstraining.leeds.ac.uk/).

## Student profile

The student should have an interest in atmospheric chemistry, air quality and global environmental problems, with a strong background in experimental physical chemistry or similar (e.g. physics, engineering, environmental science). Standard NERC eligibility rules apply.

# References

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