Improving understanding of tropospheric oxidation processes through chamber and field measurements of OH and other radicals and comparison with models.

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Project summary
The purpose of this project is to improve the accuracy of the photo-oxidation chemistry within air quality and climate models, which in turn will lead to an improved confidence in their use to predict the impact of changing natural and anthropogenic emissions into the atmosphere. Photo-oxidation in the troposphere is highly complex, and is initiated by short lived radical species, such as the hydroxyl radical, OH, but recent evidence also shows an important role for chlorine atom chemistry, even in urban areas. In this project we will deploy state-of-the-art FAGE laser instrumentation for the measurement of a range of radical species (e.g. OH, HO$_2$, RO$_2$ and OH reactivity) in the versatile HIRAC simulation chamber at Leeds. Systems for study will include isoprene, the most highly emitted hydrocarbon on the planet, whose oxidation chemistry is still uncertain, and also oxidation of aromatic species. Where opportunities arise, the project will also involve field measurements on the ground and aboard the NERC BAe146 instrumented aircraft, involving wide collaboration with other Universities. The datasets generated of radicals and other species will be compared with calculations using a box model incorporating the detailed Master Chemical Mechanism, which was developed at Leeds.

Background
The international societal response to deteriorating air quality and the changing climate is guided by the predictions of numerical models. These models contain estimates of future emissions of trace gases and aerosols from natural and human activity, their dispersal throughout the atmosphere, and their chemical transformations into a wide range of secondary products. The purpose of this project, in which you will use a combination of experimental measurements and numerical modelling, is to improve the accuracy of the photo-oxidation chemistry that is contained within air quality and climate models, which in turn will lead to an improved confidence in their use to predict the impact of changing emissions into the atmosphere. Photo-oxidation in the troposphere is highly complex, and is initiated by short lived radical species, in the daytime dominated by the hydroxyl radical, OH (Heard and Pilling, 2003). Other oxidants are also important, for example the nitrate radical (at night) and ozone. Recently, largely owing to observations of nitryl chloride (ClNO$_2$) in a wide range of locations (marine, continental, urban) (Thornton et al., 2010), the role of chlorine atoms as a widespread oxidant is becoming increasingly recognised. Many of the secondary products produced by atmospheric photo-oxidation are also directly harmful, for example ozone, nitrogen dioxide, acidic and multifunctional organic species, many of which are of low volatility and are able to partition effectively to the condensed phase, creating secondary organic aerosol (SOA), which contributes a significant fraction of tropospheric aerosol, with associated impacts on climate and human health.

Figure 1 (Left). 24 hour measurements of OH radicals in the rainforest in Borneo in April 2008 (black line) together with the basic model (yellow) and increasing recycling of OH following the oxidation of isoprene (taken from Whalley et al., 2011).

Figure 2 (Right). Global distribution of the increase in calculated OH when a model includes recycling of OH following the oxidation of isoprene (taken from Archibald et al., 2011).
Short lived radicals such as OH (lifetime < 1 sec) are ideal target species to test the accuracy of a chemical mechanism as their concentrations are controlled by the local chemistry rather than any meteorological processes. There have now been a considerable number of field campaigns in which measured concentrations of short-lived free-radicals have been compared with the calculations of models which are constrained to other measurements of longer lived species and sunlight intensity (Stone et al., 2012). Unpolluted, forested regions occupy a significant fraction of the surface of the Earth, and are characterised by large emissions of biogenic volatile organic compounds (VOCs), for example isoprene. Constrained box models using the detailed Master Chemical Mechanism and Earth System Models using more simplistic schemes calculate low concentrations of OH owing to the rapid removal by reaction with reactive plant emissions such as isoprene. Recent measurements made by our group (Whalley et al., 2011, Figure 1) and others in tropical regions show these calculations to be too low by up to an order of magnitude, and hence overestimate the lifetime of methane, a greenhouse gas, and underestimate the rate of chemical oxidation leading to secondary products including organic aerosols. These results were surprising, and inspired laboratory and theoretical studies to develop new chemistry involving OH recycling following the initial oxidation of isoprene to try to explain these results. Figure 2 shows the increase in OH calculated using a global chemistry-climate model when OH recycling is included (Archibald et al., 2011). However, the precise nature of all of the “missing” chemistry, and hence the impact on climate and air quality, is not known, despite considerable experiments in the laboratory and in simulation chambers.

In urban areas, there are still considerable discrepancies between the levels of measured radicals and those calculated by models (Stone et al., 2012), pointing to gaps in our understanding of the oxidation chemistry, which has important implications for our ability to calculate ozone production, which is a greenhouse gas and respiratory irritant, and the rate of formation of secondary organic aerosols, both of which have limit values set by regulatory legislation. Alkene and aromatic organic compounds are ubiquitous in these urban environments, and react rapidly with OH and Cl atoms, with the latter also reacting very rapidly with saturated alkanes which are more abundant.

Objectives and methodology
The specific objectives of the project are:

(1) To modify the FAGE instrumentation on HIRAC to enable measurement of the sum of organic peroxy radicals, RO₂, and to calibrate and characterise the new instrument as a function of operating conditions within HIRAC (humidity, temp, pressure, ozone, NO₂).

(2) Using both OH and Cl atoms as oxidants, to investigate the oxidation chemistry of isoprene in the HIRAC chamber, using a complete set of measurements of OH and peroxy radicals (HO₂ and RO₂), OH reactivity, and isoprene oxidation products (e.g. methyl vinyl ketone, methacrolein, formaldehyde), as a function of temperature, pressure and other conditions. The measurements will be compared with calculations using a box model incorporating the Master Chemical Mechanism to probe the skill to reproduce radicals, in particular any enhancement in OH due to recycling from isomerisation from peroxy radicals, and to probe if this is dependent on the nature of the oxidant. Collaborators will be invited to bring a wider range of instrumentation to HIRAC, for example mass spectrometric detectors, to probe a wider range of products (e.g. multifunctional VOCs).

(3) Using the same approach as in (2) to study oxidation of a range of other VOCs (for example other alkenes and aromatic VOCs) with a range of oxidants (OH, Cl, O₃, NO₃). Of particular interest is the concentration and nature of the RO₂ species generated, and to compare the measured rate of in situ ozone production with that calculated using the measured HO₂ and RO₂, and modelled using the MCM.

(4) When opportunities arise, to participate in collaborative field campaigns to measure OH, HO₂, RO₂, OH reactivity and carbonyl species using FAGE, and to operate the NCAS spectral radiometer to measure photolysis rates, either within the ground-based container or the NERC BAe-146 aircraft. Tasks would include instrument preparation and calibration, deployment and optimisation of instruments in the field, data analysis and workup, and running box models incorporating the MCM to compare with radical measurements.

(5) To collaborate with colleagues in the School of Earth and Environment, and other institutions, to incorporate updated chemistry resulting from the project into chemistry-climate models to investigate regional and global impact.
In this exciting project you will join the team who use state-of-the-art instrumentation that is used for the measurement of several radical species and other short lived intermediates. The OH radical is measured using the extremely sensitive Fluorescence Assay by Gas Expansion (FAGE) technique (Heard and Pilling, 2003), HO$_2$ by conversion first to OH, and organic peroxy radicals (RO$_2$) using a pre-reactor to convert to HO$_2$ which is measured (Whalley et al., 2013). OH reacts with many species and its total rate of removal in the system under study is measured using the OH reactivity instrument (Edwards et al., 2013). We have participated in 26 field campaigns worldwide since 1996, including deployment in Antarctica, West Africa, Tasmania, Borneo, Canada and Cape Verde. We recently made measurements in Central London during the Olympics in the ClearFlo campaigns. Measurements are made on the ground using the FGAM FAGE container (Figure 3) and aboard the NERC FAAM BAe-146 instrumented aircraft), Figure 4, which are facilities funded by the National Centre for Atmospheric Science which is based in Leeds. The Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC) is a NERC funded atmospheric simulation chamber (volume ~2.25 m$^3$) developed to bridge the divide between the study of elementary reactions in the laboratory, and large scale field work, and is shown in Figure 5 (Glowacki et al, 2007). Unlike any other atmospheric simulation chambers, HIRAC allows researchers the unique ability to control temperature (227-321 K), pressure (0-1 atm) and it is equipped via a variety of photolysis lamps to control the generation of radicals (OH, Cl) from a range of precursors (OH, O$_3$ and NO$_3$ can also be generated under dark conditions). HIRAC has a broad range of instrumentation, for example an FTIR, gas chromatographs and a variety of commercial analysers (O$_3$, NOx, CO, H$_2$O vapour, radiation) so that we can accurately monitor the chemistry occurring inside the chamber. HIRAC is equipped with a dedicated FAGE instrument to measure OH and HO$_2$ radicals, and this project will also utilise measurements of RO$_2$, OH reactivity and the carbonyl species HCHO and glyoxal using FAGE. HIRAC is also able to measure HIRAC is a member of the EUROCHAMP (Integration of European Simulation Chambers for Investigating Atmospheric Processes) network of European chambers. An advantage of HIRAC is that via the EUROCHAMP consortium and other routes, it is possible to deploy additional instrumentation at the chamber (for example mass spectrometers) to probe a wide range of trace gases or aerosols.

You will compare measurements made in HIRAC or during fieldwork with calculations from a range of computer models, in particular a box model utilising the detailed Master Chemical Mechanism (MCM), which was developed at Leeds (Saunders et al., 2003). In order to adequately describe the photo-oxidative degradation of the large number of the VOCs present in the atmosphere, models need to be extremely complex, with mechanisms often containing many thousands of reactions and chemical species. The MCM is a near-explicit chemical mechanism describing the detailed gas phase tropospheric degradation of methane and 143 primary emitted non-methane VOCs, which include the major emitted anthropogenic species as listed in the UK National Atmospheric Emissions Inventory (e.g. Saunders et al., 2003). The current version (MCMv3.2) contains ca. 6,700 species and 17,000 reactions (Jenkin et al., 2012). We have a range of platforms (Kineticus, AtChem and Facsimile) to run the MCM, and tools to extract the necessary mechanism depending on the species under study, and further tools to diagnose the model output (rate of production analysis, reactive flux tracing). The level of agreement with models is an excellent test of how well we understand the chemistry of our atmosphere for different environments.
Potential for high impact outcome

The project will deliver improved mechanisms for the oxidation of a range of important VOCs, for example isoprene and aromatics, which will lead to more accurate simulations of climate and air-quality related trace gases and aerosols. The work will be of particular interest to the Department of Energy and Climate Change, and the Department for Environment, Food and Rural Affairs, and will also provide an ideal vehicle for Science in Society activities, for example presentations in Schools. The results from the project will be disseminated to the scientific community through high quality publications in leading journals and at international conferences.

Strategic fit to National Science themes and potential to yield high quality research outputs

This project will lead to an improved representation of chemical oxidation processes within models for calculating climate and health related trace gases and particles, which is controlled by OH and other oxidants, leading to improved predictive capability of atmospheric composition and climate regionally and globally. The project directly addresses several NERC strategic challenges listed in Next Generation Science for Planet Earth 2007-2012, including in the Climate System theme: “Improve understanding of how physical, biological and chemical systems interact to change the Earth’s climate, and how these processes can be represented in global and regional climate models”, and “Determine the likely interactions between climate change and air quality”, in the Environment, Pollution and Human Health theme: “Develop better models of the behaviour and persistence of chemicals and radionuclides in the environment”, in the Earth System Science theme “Build knowledge of how atmospheric composition is controlled and feeds back to global change” and in the Technologies theme: “Develop a base of skilled people in crucial areas and monitor emerging technologies and new ideas. There have been several high impact journal publications on topics related to OH and Cl atom oxidation of VOCs (for example in Nature and Science), and further advances to solve long-standing uncertainties (e.g. isoprene) will result in dissemination with high impact.

Training

You will work in well-equipped laboratories and be part of an active, thriving and well-funded atmospheric chemistry community within the School of Chemistry, which contains the groups of Professors Dwayne Heard, John Plane and Paul Seakins, who are part of the successful Atmospheric and Planetary Chemistry
research group. The group also contains three Fellows funded by the National Centre for Atmospheric Science (NCAS), Drs. Mark Blitz, Trevor Ingham and Lisa Whalley. The School 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). Activities in these three areas are intimately linked and interdependent, providing a significant advantage. 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 broad spectrum of experience in the use of high power lasers, vacuum systems, optics, computer controlled data acquisition systems and numerical calculations.

Partners and Collaborations
You will work within a large well-funded group that has close links with the UK and international atmospheric communities. We are part of the Institute for Climate and Atmospheric Science (ICAS) here at the University of Leeds, and have close links with ICAS colleagues in the School of Earth and Environment. We also work closely on a number of joint NERC funded projects with the Universities of York, Birmingham and East Anglia, and any fieldwork in this project would be undertaken as part of a consortium of partners from around the UK, and possibly including international partners. The Leeds FAGE (fluorescence assay by gas expansion) field instruments are part of the Facility for Ground-Based Atmospheric Measurements (FGAM) of the National Centre for Atmospheric Science (NCAS), which is hosted in Leeds. The HIRAC chamber is part of the EUROCHAMP (Integration of European Simulation Chambers for Investigating Atmospheric Processes) network of European chambers.

References