Understanding the chemical formation and impact of nitrogen containing aromatic species in China

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The majority of the World's population lives in heavily urbanized areas impacted by high levels of pollution, which can have severe detrimental effects on air quality and human health. A recent study showed that around 4,000 people die each day in China as a result of exposure to air pollution (Rohde and Muller 2015). Megacities, large densely populated urban regions, often suffer from particularly high concentrations of air pollutants due to a high density of emission sources such as road traffic and regional biomass burning. One such example is Beijing, a Chinese megacity with a population of > 20 million, whose air quality problems are well documented in the media (Fig. 1). Although Beijing's air quality has improved in recent years, some important pollutants are still above recommended guidelines (in particular particulate matter (PM), ozone and NO_2). Therefore, it is important to understand what factors are controlling urban air quality so that we can formulate appropriate strategies to mitigate these problems.

Figure 1 *– Beijing sunrise. High levels of emissions coupled to photo-chemistry produce severe haze events of photochemical smog, impacting on air quality and human health.*

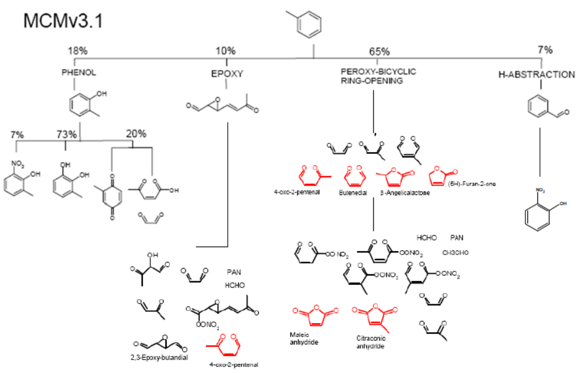

Figure 2 *– Schematic of major ring opening and retaining compounds formed in toluene chemistry in the Master Chemical Mechanism (Bloss et al., 2005). Phenolic chemistry is represented on the left side.*

During the recent Air Pollution and Human Health in a Chinese Megacity (APHH) measurement campaign in Beijing, it was observed that oxidised organic material accounted for up to 90% of the total particulate organic mass during the winter. This material is most likely formed via the oxidation of volatile organic compounds (VOCs) in the atmosphere to form secondary organic aerosol (SOA). Aerosol mass spectrometry (AMS) identified the main sources of organic particulate matter as coal combustion, cooking, biomass burning and oxidised material. Analysis of particle samples collected in Beijing during this time indicates that nitrophenol compounds make up a significant fraction of the observed organic mass. Nitrophenols are compounds containing an aromatic ring, with a phenolic OH group and a nitro (NO_2) group attached to the ring (Fig 2). These compounds are formed from the oxidation of aromatic species, with possible sources including petrol and diesel exhaust emissions (Bloss et al., 2005) and biomass burning (Finewax et al., 2018). The amounts observed in Beijing are much higher than in previous urban studies and the sources of these compounds are unclear. This material not only adds to aerosol mass, but may also impact human health as a potential carcinogen, ecosystems as a phytotoxin and climate as a source of brown carbon.

The overall aim of this project is to study the detailed formation and degradation mechanisms of atmospherically important nitrophenol compounds through the design and analysis of comprehensive chamber simulation experiments carried out at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences indoor atmospheric simulation chamber facility in China.

Objectives

- ***Improve phenolic chemistry in the Master Chemical Mechanism (MCM).***
- ***Design optimized chamber conditions for the simulation chamber experiments.***
- ***Carry out chamber experiments on phenolic and naphthalene oxidation under polluted conditions relevant to Beijing and other polluted Chinese megacities (OH/NO_x and NO_3 chemistry).***
- ***Evaluation and optimization of aromatic chemistry represented in the MCM.***

You will work closely with leading experts in atmospheric chemical mechanism development, detailed chemical modelling, chamber simulation experiments and aerosol composition measurements in York and China. Expert supervision will ensure appropriate support and guidance. This project is spilt into two linked parts:

(1) Mechanism Development and Experimental Design

Despite the importance of tropospheric aromatic oxidation processes to air quality and the associated consequences for human health, the detailed mechanisms, which are crucial components of air quality models, are still poorly understood (Bloss et al., (2005)) . In this project, a key objective is to improve our understanding and representation of key phenolic oxidation chemistry in the Master Chemical Mechanism (MCM: http://mcm.leeds.ac.uk/MCM). New detailed chemical schemes for phenolic degradation pathways (see Fig 2) will be developed and updated based on the results of recent studies. The performance of the new mechanisms will initially be evaluated against the current MCM, in terms of ability to represent the formation of ozone, NO_x and measured oxygenated organic products, with the results used to further optimize the schemes.

The new chemical schemes will be incorporated into chamber specific box models to help design the experiments in the chamber for a range of representative conditions. This will allow an initial assessment of the sensitivity of the systems to factors such as absolute and relative concentrations of VOC and NO_x and the experiment duration. It will also allow a prediction of the concentration-time profiles of specific products and product classes to ensure appropriate sampling procedures are used and that detection limits are exceeded.

(2) Chamber Experiments

The most abundant nitrophenols observed in Beijing aerosol samples were 2-nitronaphthol, 4-nitrophenol and 2-methyl-3-nitrophenol. We will study their most likely VOC precursors based on known reaction schemes; phenol, benzaldehyde, methyl-phenols, and naphthalene. In addition, we will do a small number of experiments using dihydroxy-aromatics since these were also observed in Beijing and are used as biomass burning tracers. We will simulate both the daytime oxidation by OH radicals in the presence of NO_x and night-time oxidation by nitrate radicals in the chamber.

Two sets of chamber experiments will be carried out in August 2019 and January 2020. This studentship will include the opportunity to visit the chamber in Guangzhou and play an active role in the experiment design. The chamber is a highly instrumented reactor housed in a temperature-controlled enclosure equipped with black lamps as the light source (Wang et al., (2014)). The gas-phase oxidation of the aromatic precursors will be followed using a broad range of instrumentation. From these experiments we will gain a detailed understanding of the sources and formation processes of nitrophenols and secondary organic aerosol from the atmospheric oxidation of aromatics and phenolic species under conditions observed in the Beijing urban atmosphere, including the role that day vs. night-time chemistry plays in their chemical evolution.

Potential for high impact outcome

As well as identifiable significant scientific outcomes of the project, there are potentially wider societal impacts. Improvements to the description of aromatic and phenolic compounds in the Master Chemical Mechanism will allow more accurate modelling of ozone and secondary processes such as particle formation. This is particularly important for China, where poor transport fuel quality leads to high emissions of aromatic compounds to the atmosphere. Improvements in air quality can lead to large economic benefits through improved health of the population and thus greater productivity and lower health care costs. Businesses will benefit, particularly those that are directly or indirectly affected by air pollution control measures. The MCM is a highly regarded flagship facility for atmospheric science in the UK. It is now internationally recognized as the "gold standard" benchmark mechanism, extensively used in a wide variety of science and policy applications where chemical detail is required to assess issues related to air quality and climate

This work will lead to multiple high-impact publications, presentations to international conferences and stimulate new collaborative research and knowledge exchange between the UK and China.

Training

You will work under the supervision of Dr Andrew Rickard, Dr Jacqui Hamilton and Dr Pete Edwards at the University of York Department of Chemistry (YDC). You will be based in the Wolfson Atmospheric Chemistry Laboratories (WACL), a world leading facility bringing together experts in atmospheric measurements, Earth system models and lab-studies to form the largest integrated UK atmospheric science research team. This project provides a high level of specialist scientific training in: chemical mechanism development, data analysis; chamber experiment design and interpretation, chemical compositional measurement techniques (gas and aerosol) and computational methods (MCM chamber and field box modelling). Dr Rickard has research interests that span mechanistic chemistry of complex gas- and condensed- phase systems, kinetic modelling of complex processes and the chemistry of reactive radical intermediates. He currently curates the internationally renowned Master Chemical Mechanism. Dr Hamilton and Dr Edwards have a wealth of expertise on the measurements of gas and aerosol phase composition, radical reactivity and kinetics, detailed constrained box and global modelling, and together with the WACL team will provide comprehensive training in all techniques and instrumentation required.

The student will also work closely with the group of Prof Xinming Wang at GIG, who will supervise the simulation experiments and assist in the interpretation of the data from the instruments affiliated to the chamber. This project also provides a link to the EUROCHAMP-2020 project (www.eurochamp.org) which integrates the most advanced European atmospheric simulation chambers into a sustainable world-class infrastructure for research and innovation.

This studentship is offered as part of the Leeds/York Chemistry PANORAMA Doctoral Training Programme that will provide training in addition to that offered by YDC (iDTC). These courses specifically aid your development throughout the PhD, improving transferable skills, putting research into a wider scientific context and preparing for thesis presentations and viva. The University of York and the wider NERC PANORAMA DTP provide comprehensive training programmes for students throughout their PhD studies, with a range of courses on both hard and soft skills (e.g. improving transferable skills, putting research into a wider scientific context and preparing for thesis presentations and viva). Dr Rickard also works for and with the National Centre for Atmospheric Science (NCAS), and thus the student will have access to the wider resources that NCAS provides.

You will also have access to training provided by NCAS such as the Arran instrumental Summer School, the Earth System Science Summer School (ES4), and other specialist courses on scientific computing and modelling.

Student profile

You will have a strong background in the physical sciences (good degree in chemistry, physics or similar scientific discipline), and a keen interest in environmental issues. The project will involve working in China (Guangzhou). We appreciate that this PhD project encompasses several different science and technology areas, and we do not expect applicants to have previous experience in many of these fields. The project is very well supported with experienced scientists and training in these new techniques and disciplines is all part of the PhD.

References

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