Does nighttime chemistry of isoprene impact air quality in polluted environments?

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Exposure to poor air quality is the top environmental risk factor of premature mortality globally. It is estimated that 91 % of the world's population lives in places where air quality exceeds World Health Organisation guideline limits and that 1 in 9 deaths globally are a result of exposure to air pollution. Volatile organic compounds (VOC) are emitted to the atmosphere from both man-made and natural sources. They play a key role in the formation of ozone, a toxic pollutant, and they can also increase the amount of particulate matter, through the formation of secondary organic aerosol (SOA) (Hallquist et al., 2009).

Isoprene constitutes nearly half of all global emissions of VOCs to the atmosphere, with a flux of ~600 Tg per year. The dominant source of isoprene is biogenic emissions from trees and plants, with a small emission in gasoline vehicle exhaust. In remote regions, isoprene can dominate the formation of secondary organic aerosol (Robinson et al., 2011). However, the contribution of isoprene to secondary organic aerosol formation is still under debate, especially in regions where biogenic emissions combine with those from urban environments. The interaction of isoprene with man-made pollutants, such as NO_x and sulfate aerosol, can increase the amount of toxic pollutants that can form in urban areas. A recent study of 28 megacities, found urban green spaces (Fig 1) covered on average 31 % of the built up area, ranging from 3 % (Karachi) to 58 % (London) (Huang et al., 2017). Therefore, there is potential for significant isoprene emissions in urban areas.

Recent aircraft observations of polluted power plant plumes that had mixed with air containing high levels of isoprene, found that the isoprene reactions with nitrate radicals during the night was a much more efficient source of secondary organic aerosol than previously thought (Fry et al., 2018). One possible explanation for the discrepancy between these measurements and previous laboratory results is that the atmospheric lifetime of isoprene derived peroxy radicals in these plumes could be significantly longer than has been replicated in the lab, and could lead to previously unknown reactions dominating. In order to investigate this exciting new chemistry, a series of experiments were carried out at the highly instrumented SAPHIR outdoor atmospheric simulation chamber (Fig 2) in the summer of 2018. The data from these experiments will be used during this PhD to challenge our understanding of this understudied aspect of atmospheric chemistry and also to plan and deliver follow up experiments at SAPHIR. This project will also investigate the formation of SOA from isoprene at night in a range of polluted environments using state of the art mass spectrometry. Understanding the interplay between highly reactive biogenic emissions such as isoprene and anthropogenic emissions is crucial if we are to reduce secondary pollutants such as ozone and aerosols in highly populated urban areas.

Fig 1: Poor air quality day in Beijing in summer 2017. Beijing has more than 45 % urban green space.

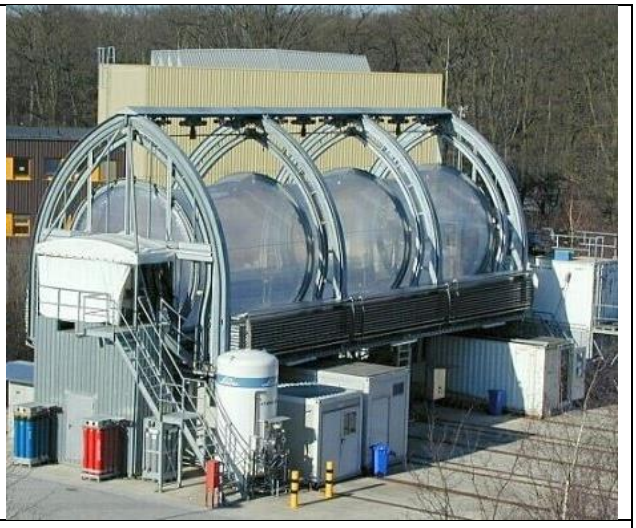

Fig 2: The SAPHIR atmospheric simulation chamber at Forschungszentrum in Julich

Project description and aims

This project aims to understand the impact of nighttime chemistry of isoprene on air quality in polluted urban and rural environments. Isoprene is emitted by plants during the day, peaking around midday, and reacts predominantly with hydroxyl radicals, which are formed in the presence of sunlight. However, a significant fraction of isoprene can still be present after the sun has set and reaction with nitrate radicals, which have higher concentrations at night, can become the main loss route. This chemistry leads to the formation of organic nitrates, which can then undergo condensation and further reactions to form SOA.

This project will use both experimental atmospheric simulation chamber data and ambient monitoring to investigate the reactions of isoprene with nitrate radicals and how this leads to increased levels of toxic pollutants. This will be achieved through the following:

1) Using simulation chamber experiments to investigate the nighttime chemistry of isoprene with nitrate radicals under polluted conditions.

The aim of the 2018 experiments at SAPHIR was to more accurately replicate the fate of isoprene peroxy radicals, compared to previous studies that have usually been carried out at unrealistically high concentrations. The student will analyse and interpret experimental results obtained using state of the art instrumentation from world leading institutions in Europe and the US. They will construct a detailed chamber specific box model incorporating the Master Chemical Mechanism (mcm.leeds.ac.uk/MCM) to evaluate and interpret the chemistry and optimise/improve the mechanism based on the results. The student will then use the results of the chamber model to design a new set of experiments to be carried out at SAPHIR during the project.

2) Quantify the contribution of isoprene nitrate secondary organic aerosol to particulate matter in polluted atmospheres and determine the key factors that control the impact of this chemistry on air quality.

Particle samples collected in a range of polluted urban and rural environments will be analysed to determine the concentrations of isoprene nitrate tracer molecules using ultra

high-resolution mass spectrometry. This state of the art analytical method has greater sensitivity than previous measurements, allowing the formation and loss of isoprene nitrate aerosol to be studied throughout the night. Particle samples are already available for a number of megacities and the student will have the opportunity to participate in fieldwork collection of aerosols during upcoming projects in Guangzhou in China and in London.

Training

This project will be supervised by Dr Jacqui Hamilton and Dr. Pete Edwards at the University of York Department of Chemistry (YDC). The successful PhD student will have access to a broad range of training workshops put on by the University of York as part of its Innovative Doctoral Training Program. The studentship is offered as part of the PANORAMA Doctoral Training Program, which provides additional training. Through the Department of Chemistry, University of York and PANORAMA training there are a wide range of activities including courses aimed at specific scientific objectives, improving transferrable skills, completing your PhD and putting your work into a wider scientific context.

Dr Hamilton, an expert in the compositional analysis of atmospheric aerosols, will provide comprehensive training in advanced mass spectrometry and data analysis strategies. Dr Pete Edwards has expertise in interpreting complex gas phase measurements with chemical modeling, and will provide training on the chamber modeling, experiment design and isoprene chemistry. This studentship 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. These were established in 2013 and comprise a state of the art 1200 m^2 dedicated research building, the first of its kind in the UK. The Laboratories are operated as collaborative venture between the University of York and the National Centre for Atmospheric Science (NCAS), co-locating around 40 researchers from seven academic groups and from NCAS. The Laboratories are also home to independent research fellows, postdoctoral researchers, PhD students and final year undergraduate research projects.

The student will have the opportunity to present their work to the scientific community at national and international meetings and conferences. They will also be encouraged to take part in outreach events organised by both WACL and NCAS in order to disseminate the research beyond the immediate scientific community (e.g. to policymakers and the general public).

Applicants should have a First or 2:1 degree in Chemistry, Physics, Computing, Environmental Sciences or a related discipline, or have a 2:2 degree and also a Masters qualification. We appreciate that this PhD project encompasses several different science and technology areas, and we don't expect applicants to have 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.

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Suggested reading

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