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The Impact of Isoprene Emissions on Air Quality in China

Yanhui Liu (1), Claire Reeves (1), Stephen Dorling (1), Graham Mills (1), James Lee (2), James Hopkins (2), Joe Acton (3), Lisa Whalley (4), Eloise Slater (4), Ben Langford (5), Eiko Nemitz (5), Qiang Zhang (6), and Ruili Wu (6)

(1) School of Environmental Science, University of East Anglia, Norwich, United Kingdom , (2) Department of Chemistry, University of York, York, United Kingdom , (3) Lancaster Environment Centre, Lancaster University, Lancaster, United Kingdom , (4) School of Chemistry, University of Leeds, Leeds, United Kingdom , (5) Centre for Ecology & Hydrology, Edinburgh, United Kingdom , (6) Department of Earth System Science, Tsinghua University, Beijing, China

Isoprene, primarily emitted by vegetation, is considered to be the most important biogenic volatile organic compound (BVOC) in the troposphere due to its abundant emission ($\sim$40% of total VOCs globally) and high ozone (O_3) formation potential. Once it is released to the atmosphere, isoprene is rapidly oxidised to form peroxy radicals (RO_2), which can react with nitric oxide (NO) to form nitrogen dioxide (NO_2), which when photolysed can form O_3. However, a minor branch of the RO_2 and NO reaction yields stable isoprene nitrates (INs) that temporarily terminate the O_3 production by tying the active nitrogen into the nitrate functional group. The lifetimes of some of these nitrates are relatively long (days to weeks), so they can be transported and destroyed away from the source, releasing NO_2 back to the atmosphere downwind. In other words, the formation of INs can change the O_3 distribution. The role of INs in NO_X ($NO + NO_2$) recycling is poorly understood, in part due to a lack of field measurement of the individual INs.

Individual IN isomers derived through different isoprene initial-oxidation pathways (OH and NO_3) were measured with a gas chromatography / mass spectrometry analytical system in the summer of 2016 in Beijing as part of the Air Pollution and Human Health in a Developing Megacity (APHH-Beijing) programme. A regional chemistry transport model (Weather Research and Forecasting model coupled with Chemistry, WRF-Chem) has been set up to simulate the isoprene oxidation processes during the campaign period for most of China. Since existing chemical mechanisms coupled to WRF-Chem represent the INs as lumped organic nitrates, we developed a more explicit chemical mechanism with 7 IN isomers by adding the Mainz Isoprene Mechanism (MIM2) and aspects of the Master Chemical Mechanism (MCM) to the Model for Ozone and Related chemical Tracers (MOZART-4) mechanism.

The measurement data from Beijing have been used to evaluate and improve our understanding of the production and loss of the INs. The modelled diel patterns of INs agree well with the observations, although there are discrepancies in the absolute concentrations. The impact of isoprene on O_3, NO_X, NO_Y and HO_X in different regimes across China is discussed in terms of the NO_X-isoprene ratio as well as the role of isoprene derived organic nitrates in NO_X recycling. The amount of NO_X recycled through the INs is quantified by using a tagging method. We also examine how different treatments of isoprene and the INs in reduced mechanisms affect the results, including the sensitivity of the formation of INs to the RO_2 cross-reactions.