Long-term trends in oxidant budgets of the northern hemisphere constrained by alkanes and alkyl nitrate ratios.

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Abstract:

Our study aims to understand how the concentrations of ozone ($O_3$) and hydroxyl radicals (OH), and as such the tropospheric oxidizing capacity, have changed since the mid-20th century, largely as a result of anthropogenic emissions. We do this through a combination of field observations and numerical simulations. Global emissions of $O_3$ precursors, such as volatile organic compounds (VOCs), oxides of nitrogen ($NO_X$) and carbon monoxide (CO), have changed substantially since preindustrial times, resulting in changes to the tropospheric budgets of $O_3$ and OH. However, the absence of long-term observational records of $HO_X$ and $NO_X$ results in large uncertainties associated with the current understanding of these past changes.

We use measured long temporal variations of alkane and alkyl nitrate concentrations from firn air to constrain global atmospheric model scenarios, because the formation of nitrates from alkanes is closely linked to chemistry involving $HO_X$ and $NO_X$. This enables us to assess changes in the $O_3$ and OH radical budgets of the northern hemisphere troposphere. We have used the UK community global chemistry-climate model (UKCA) in its current configuration as part of the UK community Earth System Model (UKESM-1) to carry out transient model experiments from 1960 to the present day. We use global emissions data from the CMIP5 and also from the forthcoming CMIP6 model intercomparison projects. CMIP6 emissions show significantly higher $NO_X$ and C3-C5 alkane fluxes compared to CMIP5, resulting in increased nitrate formation. The model is validated with surface and airborne observations of $O_3$ precursors, alkanes and alkyl nitrates, as well as with long-term trends for alkanes and nitrates obtained from firn air in Greenland ice cores.