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Measurements and modelling of OH and HO_2 during TORCH 2003 and 2004

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Short-lived free-radicals play a crucial role in determining the composition of the atmosphere. Their concentrations are determined by *in situ* chemistry and not by transport, and hence provide ideal targets for the predictions of box models based on our current understanding of tropospheric oxidation mechanisms. Measurements of the concentrations of OH and HO_2 radicals were made using Fluorescence Assay by Gas Expansion (FAGE) on 23 days during each of the Tropospheric ORganic CHemistry (TORCH) field campaigns at Writtle College, Essex, in July-August 2003, and at the Weybourne Atmospheric Observatory, Norfolk, in April-May 2004. Writtle is located $\sim$ 20 miles east of London, allowing sampling of the London plume as well as polluted air originating from Europe. Weybourne experiences clean air from the North Sea and more polluted air masses, including a more aged London plume.

The presentation will give an overview of the data along with an analysis in the context of simultaneously measured free-radical sources and sinks for a variety of airmass types at the two sites. Box modelling based on the Master Chemical Mechanism (MCM (version 3.1)) has been used to calculate the concentrations of OH and HO_2 radicals for comparison with measurements for both campaigns. For the 2003 Writtle experiment, the model is able to capture the diurnal variation of both radicals and the absolute agreement is also good. For HO_2, better agreement is observed if significant uptake of HO_2 radicals onto aerosols (mainly organic in nature) is included in the model. Preliminary modelling of the 2004 Weybourne data shows the model is able to capture the shape of the OH profile but appears to under-predict absolute levels.

Modelling for HO_2 does not currently show the same level of agreement as seen in the 2003 Writtle experiment, although uptake of HO_2 onto aerosols has yet to be included in the chemical mechanism.

The Leeds OH lifetime instrument was also deployed during both TORCH campaigns to make a direct measurement of the total OH loss rate (the inverse of its atmospheric lifetime). When combined with calculations of the rate of production of OH (from measurements of the rate of photolysis of ozone, reaction of HO_2 with NO and other routes) the OH lifetime can be used to calculate steady state OH concentrations, and these are compared with the FAGE measurements. The MCM has also been used to calculate the rate of OH loss and comparison with the measured values reveals a significant discrepancy, suggesting the loss rate of OH is underestimated by $\sim$ 40%.