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Measurements of the OH lifetime during TORCH 2003 and 2004

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Comparison of measured hydroxyl radical (OH) concentrations with model predictions constitutes a stringent test of the accuracy of chemical mechanisms describing tropospheric oxidation. However, when there are discrepancies, e.g. modelled OH is higher than measured, it is not clear whether the OH sources are overestimated or the OH sinks are underestimated. Direct measurement of the total OH loss rate (the inverse of its atmospheric lifetime) due to reaction with its sinks provides an additional constraint for the model.

A field instrument for measurement of the chemical lifetime of OH in the atmosphere has been developed and characterised at Leeds. Ambient air is drawn at a flow rate of 300 slm at atmospheric pressure through a 10 cm i.d. flowtube which contains a motorised, translatable injector, in which OH is produced by 184.9 nm photolysis of water vapour, and then injected into the main flow. The OH concentration is measured downstream of the injector using laser-induced fluorescence at low pressure, and by stepping the injector away from the OH detection point, the decay of OH with distance is measured. Knowledge of the flow-velocity within the flowtube enables the total OH loss rate to be measured.

The lifetime instrument was deployed in the two Tropospheric ORganic CHemistry (TORCH) field campaigns at Writtle and Weybourne in 2003 and 2004, respectively, and a detailed laboratory characterisation has also been performed. This presentation will describe the technique and its characterisation along with the field observations of the OH lifetime and a discussion of the observed correlations with measured con-

centrations of the major sinks of OH (e.g. NO_2 and acetylaldehyde). A significant ($\sim$ 30%) underestimate of OH sinks was found in both TORCH campaigns. When combined with measurements of the rate of production of OH (for example from ozone photolysis and the HO_2 + NO reaction), the OH lifetime can be used to calculate steady-state OH concentrations, and these are compared with measurements using Fluorescence Assay by Gas Expansion (FAGE). A zero-dimensional box model based on the Master Chemical Mechanism has also been used to calculate the OH lifetime, and a comparison with the measurements suggests that the model is under-predicting the loss rate of OH by an average of 40%.