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Quantification of Hydroxyl Radical reactivity in the urban environment using the Comparative Reactivity Method (CRM)

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Hydroxyl (OH) radicals play an important role in 'cleansing' the atmosphere of many pollutants such as, NO_x, CH_4 and various VOCs, through oxidation. To measure the reactivity of OH, both the sinks and sources of OH need to be quantified, and currently the overall sinks of OH seem not to be fully constrained. In order to measure the total rate loss of OH in an ambient air sample, all OH reactive species must be considered and their concentrations and reaction rate coefficients with OH known.

Using the method pioneered by Sinha and Williams at the Max Plank Institute Mainz, the Comparative Reactivity Method (CRM) which directly quantifies total OH reactivity in ambient air without the need to consider the concentrations of individual species within the sample that can react with OH, has been developed and applied in a urban setting.

The CRM measures the concentration of a reactive species that is present only in low concentrations in ambient air, in this case pyrrole, flowing through a reaction vessel and detected using Proton Transfer Reaction – Mass Spectrometry (PTR-MS).

The poster will show a newly developed and tested PTR-TOF-MS system for CRM. The correction regime will be detailed to account for the influence of the varying humidity between ambient air and clean air on the pyrrole signal. Further, examination of the sensitivity dependence of the PTR-MS as a function of relative humidity and $H_3O^+(H_2O)$ (m/z=37) cluster ion allows the correction for the humidity variation, between the clean humid air entering the reaction vessel and ambient air will be shown. NO, present within ambient air, is also a potential interference and can cause recycling of OH, resulting in an overestimation of OH reactivity. Tests have been conducted on the effects of varying NO concentrations on OH reactivity and a correction factor determined for application to data when sampling ambient air.

Finally, field tests in the urban environment at the University of Leicester will be shown coupled to an examination of trends in OH reactivity and other air quality markers such NO_x and black carbon.