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Investigation of the impact of higher molecular weight organics on OH reactivity in London

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Volatile organic compounds (VOCs) play an important role in the formation of pollution in the air, particularly in the boundary layer of the atmosphere. VOCs in an urban atmosphere react with radical species to form ozone (O_3), which at ground levels can pose a significant threat to health.[1] Air quality models have been developed to predict the effect of emissions on air quality. Numerous studies of urban environments show discrepancies between measured and predicted estimates of the lifetime of OH radicals. One possibility is that the magnitude of VOCs as a sink for reactive species is underestimated in models, including unmeasured and larger aromatic species.

To study some of these additional compounds we have developed a method using comprehensive two dimensional gas chromatography coupled to a flame ionisation detector (GC×GC-FID). GC×GC is a hyphenated technique where two columns are coupled together via a modulator, providing two discrete separations of each species based on boiling point and polarity.[2] This provides a high resolution method, with increased separation power and improved peak capacity when compared to many single column systems.[3]

This technique was used in conjunction with a dual channel GC (DC-GC) during the Clean Air for London (ClearfLo) project to increase the speciation of the complex air matrix. Target compounds were in the range C1 to C13+ VOCs, including oxygenates, aromatics, saturated and unsaturated aliphatics. Calculations of the pseudo first order OH reactivity indicates that higher carbon number VOCs may account for some of the missing OH sinks in comparison to emission inventory estimates. During summer measurements the role of biogenic VOCs increases, with isoprene and monoterpenes acting as important OH sinks. Including these should enhance the prediction capability of air quality models. This can then lead to the introduction of new policies for the reduction of pollution precursors and hopefully result in improved air quality.

References

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