

## Measurement of Organic Aerosol Precursors over an Oak Forest

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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### Summary

Emission fluxes of isoprene, its oxidation products, and other oxygenated VOCs were measured using eddy covariance above a mixed oak forest in southern England during summer 2005. VOC concentrations were measured using proton-transfer reaction mass spectrometry. Fluxes of isoprene and its oxidation products (MVK and MACR) followed a diurnal pattern consistent with biogenic emission from the forest canopy. Fluxes of other oxygenated VOCs followed a more complex pattern, consistent with vehicle-related sources beyond the forest.

### Introduction

Emissions of biogenic VOCs from forests can be estimated from leaf/branch measurements made using cuvettes, scaled by the use of models to encompass the range of light and temperature regimes present in a forest canopy. This combined measurement and modelling approach necessarily has to be used for estimating emissions on regional, national and global scales because of the impossibility of making field measurements of VOC fluxes across the variability represented by the earth's forests. However, it is important that such model estimates be reconciled with actual field measurements at some sites, to ensure that the model estimates reproduce the true pattern of emissions in response to a changing environment. Moreover, it is important to be sure that the models include all the relevant sources (*e.g.* leaf litter or under-storey vegetation). Direct field measurement of VOC fluxes above a forest has become possible through the development of fast-response ( $> 1$  Hz) sensors that can be used with sonic anemometry to measure fluxes using the methods of eddy covariance. This contribution reports initial flux data from measurements made above an English oak forest using Proton-Transfer Reaction Mass Spectrometry (PTR-MS) for the rapid quantification of VOC concentrations, coupled with sonic anemometry. In this study, simultaneous fluxes of ozone and aerosols were made, but only the VOC data are reported here.

### Scientific activities

The measurement site was at Alice Holt, Straits Enclosure, Hampshire (51° 7' N; 0° 51' W), a managed lowland mature oak forest (*Q. robur* and *Q. petraea*) interspersed with ~ 10 % ash (*Fraxinus excelsior*). Measurements were made during July and August 2005. Sensible heat and momentum fluxes were measured using a Gill Solent R1012A ultrasonic anemometer; VOC concentrations were measured using an Ionicon Proton Transfer Reaction Mass Spectrometer (PTR-MS). Other measurements included aerosol components (Aerodyne Aerosol Mass Spectrometer), total particle number (5-2000 nm diameter) (Condensation Particle Counter) and ozone (modified fast response GFAS sensor; [Gusten and Heinrich, 1996]).

Air for PTR-MS analysis was sampled down a 30 m Teflon tube mounted on top of a 25 m tower, from immediately below the sonic anemometer (fig 1). Standard drift tube conditions were used ( $E/N = 120$  Td), and a daily instrument background was measured using a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst heated to 200 °C. Two measurement modes were used:

1. Scanning a range of masses ( $m/z$  21 – 141) at 0.5 s/scan; scans were made at 0 and 30 minutes past the hour for 5 min;
2. 8 or 9 predefined masses ( $m/z$ ) were scanned for 25 min, including  $m/z$  21, 33, 37, 41, 45, 47, 59, 61, 69 and 71. (20 ms on  $m/z$  21 and 37, and 50 ms on all other masses). Note that masses represent  $m/z$  for the protonated analyte (MW+1).

Concentrations were calculated using reaction rate constant ( $k$ ) values from Zhao and Zhang [2004] and reaction time ( $t$ ) values were calculated from  $t = L/vd$  [Lindinger, 1998]. Fluxes were calculated using a 2 s lag time.



Figure 1. Measurement site in Alice Holt forest, showing the access tower and (inset) the PTR-MS inlet immediately below the sonic anemometer.

### Scientific results and highlights

Major emissions were isoprene, methyl vinyl ketone and methacrolein (MVK+MACR, which are not separated by PTR-MS), acetaldehyde, acetic acid, acetone and methanol. Median concentrations (20<sup>th</sup> July 2005 to 18<sup>th</sup> August 2005) were 0.10 ppb, 0.01 ppb, 0.26 ppb, 0.02 ppb, 0.38 ppb and 1.50 ppb respectively. Emissions correlated well with temperature (Figure 2).

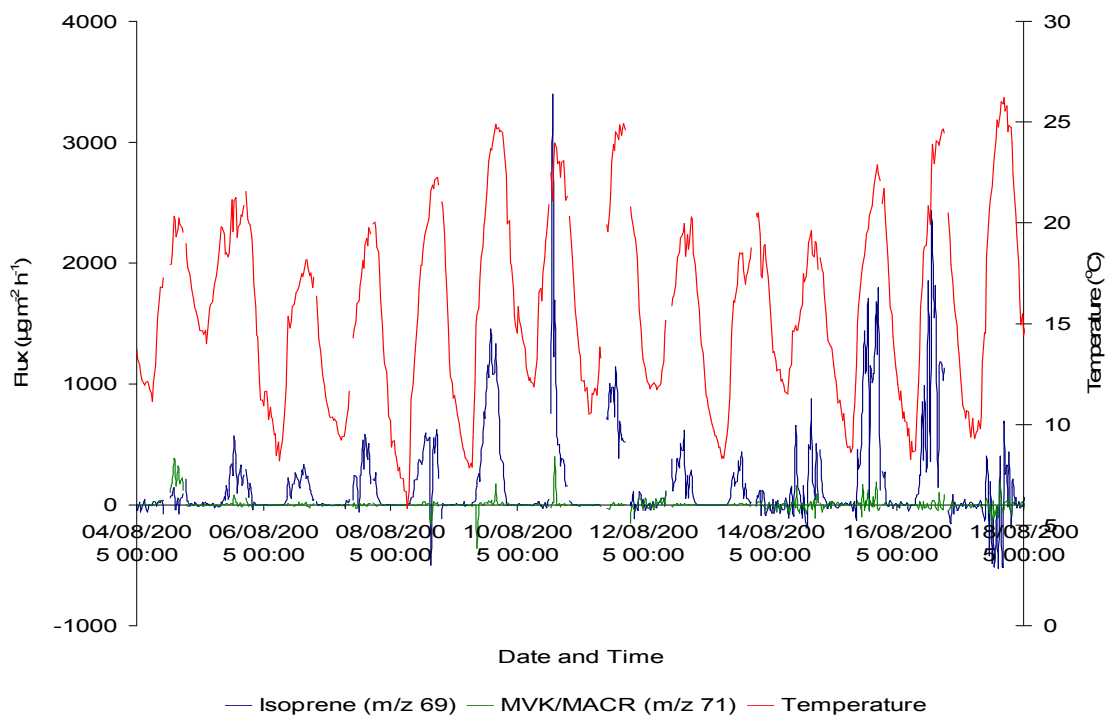


Figure 2. Isoprene and MVK/MACR flux and temperature variation, 4<sup>th</sup> August to 18<sup>th</sup> August 2005.

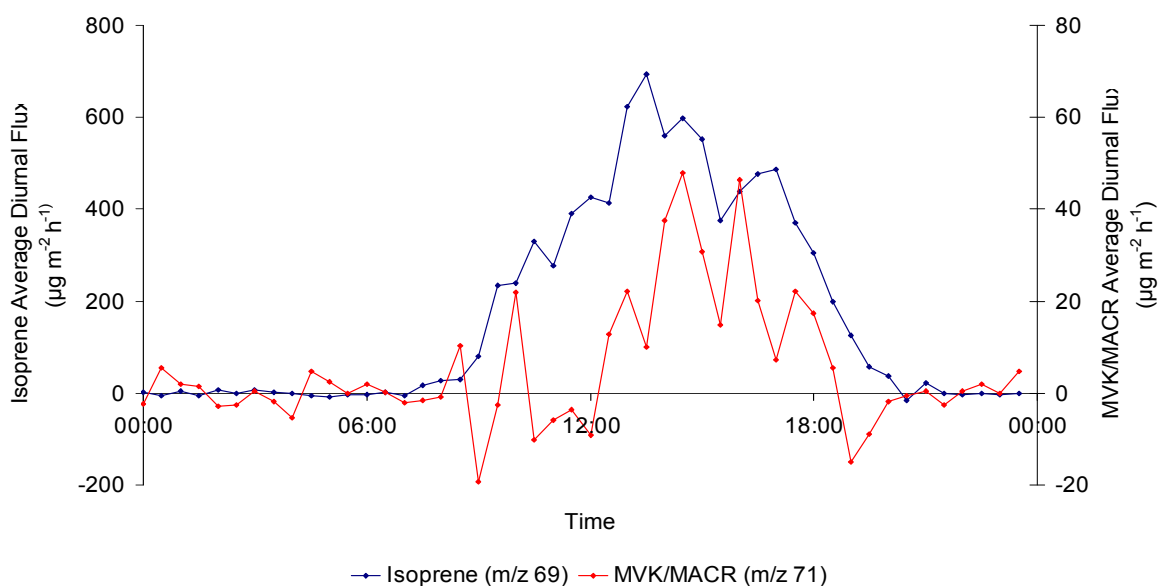


Figure 3. Average diurnal flux of isoprene and MVK/MACR, 4<sup>th</sup> August to 18<sup>th</sup> August 2005.

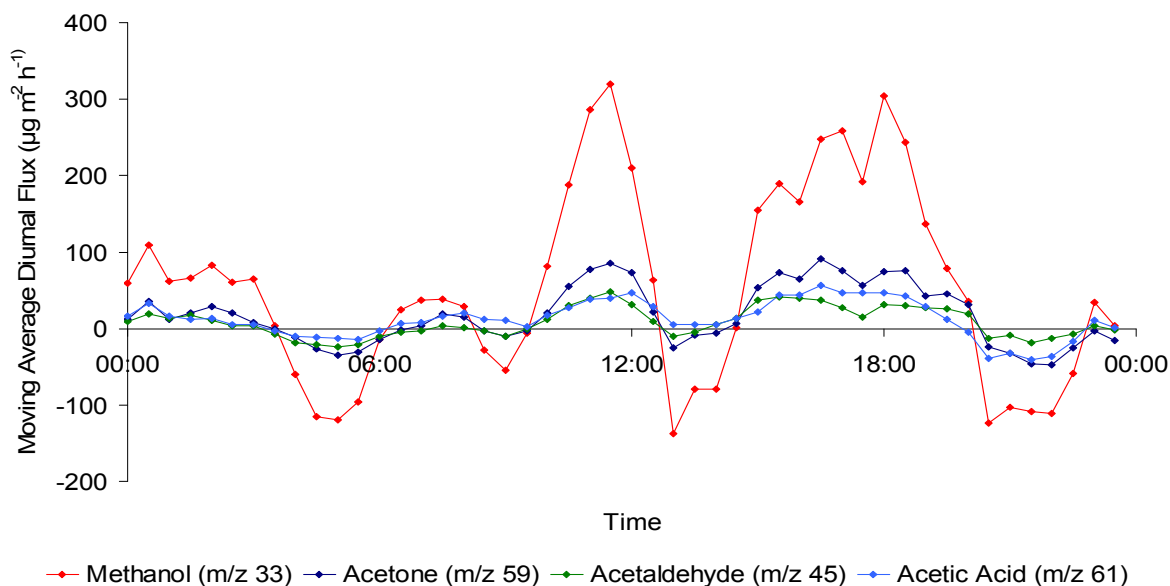


Figure 4. VOC average diurnal flux from 4<sup>th</sup> August to 18<sup>th</sup> August 2005. Probable contribution from a nearby main road.

Clear diurnal trends of all VOCs were seen (Figures 3 and 4). Although the fluxes of isoprene and its oxidation products usually followed the expected diurnal pattern, peaking in early afternoon (Figure 3), other VOC fluxes had a more complex pattern, suggesting a role for anthropogenic emissions from local road traffic (Figure 4).

### Future outlook

The results presented here are being analysed for comparison with the simultaneous fluxes of ozone and particles made by colleagues, and for a more detailed analysis of some of the signals, *e.g.* the contribution of isoprene fragments to m/z 41. An automated diffusion calibration system is being developed for a range of VOCs to permit field calibration of the PTR-MS, and a system for parallel GC-FID analysis using pre-concentration and thermal desorption has been constructed, to facilitate the assignment of individual m/z values to specific VOCs.

### References

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